



DSS FILE NO.: 14SQ.23440-5-9231
SERIAL NO.: 1SQ85-00235

**DEVELOPMENT AND EVALUATION OF
CATALYSTS FOR HYDROGENATION OF
RAW COLD LAKE PITCH**

Raj N. PANDEY, PhD

Guelph Chemical Laboratories Ltd.

330 pp

246 Silvercreek Parkway N., Guelph, Ontario, Canada. Tel. (519) 836-2313

CONTRACT SERIAL NO.: 1SQ85-00235

REQUISITION NO: 23440-5-9231

CONTRACTOR: Guelph Chemical Laboratories
Limited

Final Report

DEVELOPMENT AND EVALUATION
OF CATALYSTS FOR HYDROGENATION
OF RAW COLD LAKE PITCH

DSS File No. 14SQ.23440-5-9231

by

Raj N. Pandey, Ph.D.

Guelph Chemical Laboratories
246 Silvercreek Parkway North
Guelph, Ontario
N1H 1E7

March 28, 1988

3304P

MICROMEDIA



TABLE OF CONTENTS

	page
Foreword	iii
Abstract	vi
I INTRODUCTION	1
I.1 Background	1
I.2 Objective	4
II STUDIES IN FLASH HYDROLYSIS	
- A Literature Review	8
II.1 Experimental Approaches	16
II.2 Early Work	22
II.3 Recent and Current R & D Trends	38
II.4 Results and Discussion	50
II.5 Catalytic FHP	74
III EXPERIMENTAL	85
III.1 Setting Up Apparatus and Operation of Fast Temperature Measuring Device	85
III.1.1 Reactor systems	85
III.1.2 Calibration of Thermocouple	91
III.2 Analytical Procedure	99
III.2.1 Analysis of Pitch Samples	99
III.2.2 Analysis of FHP Products	103
IV PREPARATION OF CATALYSTS	119
V RESULTS AND DISCUSSION	123
V.1 Results of Non-Catalytic Experiments	123

V.2	Results of ZnCl_2 Catalyzed Experiments		123
V.3	Results of SnCl_4 Catalyzed Experiments		221
V.4	Results of $\text{ZnO-Cr}_2\text{O}_3$ Catalyzed Experiments		229
V.5	Results of FeSO_4 Catalyzed Experiments		240
V.6	Results of Mg-SiO_2 Catalyzed Experiments	..	258
V.7	Results of Al-SiO_2 Catalyzed Experiments	..	268
V.8	Results of P-SiO_2 Catalyzed Experiments	...	277
V.9	Results of Na-SiO_2 Catalyzed Experiments	..	283
V.10	Results of KCl_2 Catalyzed Experiments		288
V.11	Results of CaCl_2 Catalyzed Experiments		291
VI	CONCLUSION		294
VII	RECOMMENDATIONS		296
VIII	REFERENCES		302
IX	APPENDICES		310

FOREWORD

The demand for oil and gas require development of techniques for fuller conversion/utilization of available residual materials such as pitch for the production of substitute natural gas (SNG), light liquids and low char. Flash Hydrolysis (FHP), while still in the process of development, offers significant advances in technique over the conventional as it is based on severe condition of fast heating rates and short residence time. The process of conversion is based on the reaction of PNA in asphaltene and maltene fraction of the residuals with hydrogen at high temperature and pressure, high mixing rate and short residence time.

This report presents the results obtained during a study of the "Development and Evaluation of Catalysts for Hydrogenation of Raw Cold Lake Pitch". The work was performed by Guelph Chemical Laboratories Ltd, a small 100 % Canadian company dedicated to Energy research and services. The hydrogenation reaction was studied by Flash Hydrolysis (FHP) technique.

A number of individuals have made contributions during the course of this study. Eric Ingard contributed in the assembly of the fast temperature measuring device and execution of FHP runs. Greg Stachnik provided expert

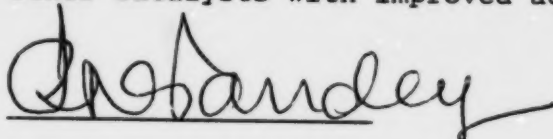
assistance in a computerized literature search and determined the properties of the pitch. Miss Pamela Dempsey, Anne Barkema, and Mrs Elizabeth McCann did the typing and the diagrams for the manuscript. The enthusiastic support of all these individuals is gratefully acknowledged.

The writer remains indebted to Dr Martin Ternan in whose continued encouragement and infinite patience the bench scale FHP facility at our laboratories has evolved and developed.

This work is continuing. It is proposed to set-up a two-stage continuous Flash Hydrolysis reactor for studying the hydrogenation of pitch. We will continue to screen various heterogeneous catalysts for their activity and selectivity for the conversion of pitch to desirable products while consuming a minimum amount of hydrogen and minimum amount of char formation.

An additional objective of the continuous FHP experiments would be the availability of sufficient sample for analyses. In a batch scale FHP experiment, frequently the analytical errors become inadmissibly high mainly due to small size (mg) of samples. Continuous FHP will certainly overcome these difficulties. Furthermore, the heat and mass transfer characteristics will be improved. In this investigation, zinc chloride emerged as the best among the catalysts examined. We will investigate the feasibility of this

catalyst further in continuous FHP and will strive to develop other catalysts with improved activity and selectivity.

A handwritten signature in dark ink, appearing to read "R. Pandey", with a horizontal line underneath the name.

Raj N. Pandey, Ph.D. Queen's
Project Manager

ABSTRACT

This report summarizes the results of CANMET research project on the "Development and Evaluation of Catalysts for Hydrogenation of Raw Cold Lake Pitch" (DSS File No. 14SQ.23440-5-9231).

The work performed during the period is presented in six sections: Literature Review; Reactor System and Experimental Procedure; Catalyst preparation; Results and Discussion; Conclusion; and Recommendations for Future Work. Considerable difficulties were encountered in handling and analyses of liquid products and are high-lighted in the appendix.

It was felt that there was an important need for a more detailed review of the literature than was originally planned. For this reason, the literature review covered exhaustively the journals, patents and technical reports. The information on literature was labouriously collected - often from dispersed technical sources. This review which is planned to be published, it is hoped, will not only be of benefit to the general and industrial reader but will also give an incentive to academic enquiry.

The hydrogenation of Cold Lake pitch was studied over KCl , $CaCl_2$, $SnCl_4$, $ZnCl_2$, $FeSO_4$, $ZnO-Cr_2O_3$, SiO_2 impregnated with sodium nitrate, magnesuim nitrate, aluminium nitrate and

phosphoric acid. The ratio of the third row element to silicon was kept 1/10. Typical FHP of pitch produces a wide range of gaseous and liquid products. The catalysts were found active and yielded gaseous and hydrogenation products in significant amounts in comparison to non-catalytic reactions. Furthermore, in catalytic FHP, the char formation was significantly reduced. The effect of process variables: temperature (300-1100 °C), heating rate (110-330 °C/s), H₂ pressure (250-1400 psig), vapour residence time (3.5-11 sec) and catalyst/pitch weight ratios (0.4-2) were also studied. The temperature vs time profile curves were constructed from oscilloscopic measurements.

A gas chromatograph in conjunction with traps, gas collecting cylinders downstream were used to provide quantitative analyses of the low boiling distillates and gases. The simulated distillation of the heavy distillate was performed by gas chromatography according to ASTM D2887.

Zinc chloride was found as the best among the catalysts examined. It yields lower char values, lower gaseous products and desirable boiling range distillates. Using ZnCl₂ as the catalyst, the highest carbon conversion of pitch to light products was approximately 93 Wt %, corresponding to 7 Wt % carbon as char. A part of this work, "Zinc chloride Catalyzed Flash Hydropyrolysis of +525 °C Pitch from Cold

Lake Bitumen", has been submitted to the Canadian Journal of Chemical Engineering for publication.

I. INTRODUCTION

This report for the CANMET/ERL contract research on the Development and Evaluation of Catalysts for Hydrogenation of Raw Cold Lake Pitch is submitted to Dr. Marten Ternan of Energy Research Laboratories. The work was conducted at Guelph Chemical Laboratories.

I.1 Background

Residual pitches constitute a large potential hydrocarbon source for distillate fuels. An upgrading/utilization method for the residual pitch is becoming important as a result of increasing demand for oil and gas and decreasing availability of lighter feed stock. The pitch residuals are mainly composed of maltenes and asphaltenes. The asphaltene fractions are known to possess a higher average aromaticity. A small percentage of heteroatom (N,S,O) are also present in the molecular weight than the corresponding maltene fraction. Asphaltene represent the most refractory and difficult portion of the heavier feed stocks to process. Chemically the molecules usually have a combination of aromatic (A), parafinics (P) and naphthnics (N) structure in addition to heteroatoms. The high aromaticity and molecular weight of residuals are attributed to the large molecules of condensed polynuclear aromatics (PNA). Thus pitch possess similar condensed PNA structure as

coal, although there are subtle differences in the chemical structures between coal-derived asphaltenes and asphaltenes derived from heavy oil residuals. The demand for oil and gas require development of techniques for fuller conversion/utilization of available residual materials for the production of substitute natural gas (SNG), light aromatic liquids and low char.

Flash hydropyrolysis (FHP), while still in the process of development, is considered to be an advanced technique over the conventional as it is based on severe conditions of rapid heating rate (10^2 to 10^6 degree/second) and short residence time. The process of conversion is based on the reaction of the PNA in asphaltene and maltene fraction of the residuals with hydrogen at high temperature and pressure, high mixing rate and short residence times. The thermal treatment causes opening of the PNA ring structure and formation of free radicals. The hydrogen is believed to participate as a diluent and as a participant in free radical chain propagation, e.g. $R \cdot + H_2 \rightleftharpoons RH + H \cdot$ forming low molecular weight hydrocarbon species and inhibiting second order polymerization or condensation reactions. By using short residence time and rapid quenching, the reaction is terminated preventing dehydrogenation, repolymerization, carbonization or decomposition. The principal reaction products are liquid, gaseous hydrocarbons and char.

Although the available literature on the fundamental information on FHP process is presently sparse, it has been recognized that the reactions occurring during FHP processes are complex. The products yields, composition and distribution is dependent on process variables such as pressure, temperature, rate of heating and residence time.

Several laboratories in the United States and Canada have been engaged in Coal Liquefaction research studies using Flash Hydropyrolysis Technique. Processes currently under development are at Brookhaven National Laboratories (BNL), the Cities Services, Rockwell International, and Occidental Research Corporation.

Flash Hydropyrolysis in the presence of catalysts may offer significant improvement in conversion efficiency of PNA's to liquid products at relatively less severe reaction conditions than non-catalytic FHP studies. The use of catalysts has not been studied in FHP process in detail in the past. An effective catalyst would crack the PNA structure and maximize product yields. It would also allow the use of milder conditions and lower hydrogen consumption. The fluidity of hydrocarbons produced in the FHP process can be increased by saturation of bonds with hydrogen. The fuel product market value is dependent on the H/C ratio. In general, market value moves upward as the fuel product

becomes lighter and the H/C ratio increases.

Our studies on catalytic Flash Hydropyrolysis of residual pitch, began with an object of the development of catalysts to convert PNA molecule in the pitch, relatively deficient in hydrogen to a more liquid form. If it appears feasible, systematic continuous flow flash hydropyrolysis studies be conducted and process developed.

I.2 Objective

The purpose of the present investigation was to develop an effective catalyst and experimental conditions under which pitch would be converted to maximum liquid yield and minimum char. For that purpose a series of experiments were conducted using different catalysts. The work program for the development of hydrogenation catalyst included the following:

1) Literature Review

The initial phase of the program involved a comprehensive literature search for the last ten years on the Flash Hydropyrolysis process of bitumen heavy residuals and coal, the yield and composition of gaseous and liquid products, and methodology for collection, sampling, extraction and analysis of gaseous, and liquid products. The sources of information used for the search were relevant literature and publications received at various Universities

and NRC libraries and communications with other researchers familiar with Flash Hydropyrolysis work. Computerized literature search facilities at University of Guelph were used.

2) Preparation and Characterization of Catalysts

An effective catalyst that will selectively crack the PNA structure to maximize the liquid yields was required. Hopefully it would also allow use of milder conditions and lower hydrogen consumption. The catalysts selected for the present study were prepared and characterized in consultation with the Scientific Authority. The catalyst used in the investigation were: ZnCl_2 , SnCl_4 , CaCl_2 , AlCl_3 , FeSO_4 , ZnO , Cr_2O_3 and SiO_2 impregnated with each of the compounds: sodium nitrate, magnesium nitrate, aluminium nitrate and phosphoric acid. The ratio of the third row element to silicon was 1/10. The impregnated materials were dried at 110°C for 10 hours and calcined at 500°C for 6 hours. Samples of all the catalysts were submitted to scientific authority.

3) Setting up Apparatus and Operation of Fast Temperature Measuring Device (Oscilloscope) and Analytical Procedure

A schematic diagram of the modified FHP unit used in the present investigation is shown in the experimental section. The experimental setup and the method of executing FHP runs were the same as that described in the earlier studies (1,33)

(R.N. Pandey, Final Report to CANMENT, August, 1984). The reactor, RT, temperature monitoring device was modified so that a temperature vs time profile could be recorded. This was accomplished by setting oscilloscope with hold feature and photographic facility which was not available in previous studies. The oscilloscope was calibrated in the experimental temperature range. A thermal conductivity detector was also installed at the reactor outlet.

Analytical Procedure

A gas chromatograph was used to provide quantitative analysis of the liquid and gas products as was done in previous work. The possible low boiling products varying from C1 to C4 were identified from the retention times of pure compounds, and the heavier hydrocarbon liquids were analyzed by chromatographic distillation (ASTM D2887).

4) Flash Hydropyrolysis Experiments

"Base Conditions" were developed using zinc chloride as catalyst. An experiment was performed at the base condition when no catalyst was present. FHP experiment was performed using each catalyst under base conditions. Five catalyst were chosen to study the effect of process variable.

Additional experiments were performed with most promising variables.

5)

Based on the product evaluation (liquid and gaseous products), best catalyst was selected.

6) FHP Experiments with Selected Catalyst

The optimum catalyst was used in subsequent FHP runs. The heating rate curve, the chromatographic distillation curves and the results are presented in the acceptable format.

7) Completion of Work, Assessment of Results and Report

This report contains:

- o Comprehensive and a critical review of the studies in flash Hydropyrolysis.
- o Detailed diagrams of all the equipment used.
- o Detailed description of the analytical procedures used.
- o All of the experimental results.
- o Conversion and product yields during Flash Hydropyrolysis, heating rate curves and chromatographic distillation curves.
- o Carefully considered explanations of phenomena observed during the FHP experiments.
- o Recommendations for additional work.
- o A detailed work statement for a follow-up study is presented.
- o A detailed design of an apparatus to continuously flash hydropyrolyze pitch is also given.

II STUDIES IN FLASH HYDROLYSIS - A LITERATURE REVIEW

In its basic form, FHP consists of the rapid heating of carbonaceous substances for a short period of time in an atmosphere of hydrogen. The heating rate is kept high enough to affect breakdown of most of the high molecular weight material to fragments of lower molecular weight. Furthermore, the pressure of hydrogen is maintained to effectively diminish the recombination of the reactive fragments formed during flash heating. The duration of the heating is kept to a minimum so as to suppress irreversible char-producing pyrolytic reactions. Thus in FHP process the usual formation of chars which cannot be converted to hydrolytic products even at very high pressure of hydrogen are inhibited. Typically the temperature ranges between 500-1000 °C, the pressure between 1000-3000 psi and the flash duration from 1-10 secs. The flash heating rate 10^2 to 10^6 °C/sec is accomplished by a variety of techniques. The desired residence time is typically attained by varying the flow rate and heating zone. Catalysts, if used, play an important role. Catalytic FHP not only becomes more effective at less severe conditions of temperature and pressure but also yields more desirable products.

Since the heating time is shorter than the reaction time it can be argued that there is low amount of reaction during

the heating period and most FHP reactions take place isothermally at the final temperature. Furthermore the variation of temperature during the flash can bring about the desired optimization via subjection of the material to succession of flashes at different temperatures. The subsequent quenching of the products allows the study of initially formed products. Carefully designed FHP experiments can thus be of value for the establishment of pathways in the conversion of materials in contrast to industrial hydropyrolysis processes which have been developed and are carried out over longer periods of time. Despite the complexity of reactions, mechanisms may be postulated for these conversions. The knowledge of such mechanisms could economically improve industrial conversion processes and enhancement in the development of present state of FHP techniques. The detection of the initially produced molecular species during hydropyrolysis is also, of course, of great interest to fundamental researchers.

This review has been limited essentially to the conversion of coal, materials rich in polynuclear aromatics (tars and pitches) and model compounds (condensed aromatic compounds) by FHP. It is recognized, however, that much valuable work has been carried out on the Flash Hydropyrolysis of natural materials - particularly on wood biomass. This work could become the subject of a further

review which could encompass comparative studies including enzymatic and hydrolytic conversions of renewable feed materials.

II.1 Chemical Pathways

Most of the studies employing FHP technique have been directed towards the conversion of coal. It is therefore appropriate to briefly begin with a general consideration of the coal as a feed. There are subtle structural differences of various type of carbonaceous feeds but all have in common condensed aromatic rings.

H. Juntgen (2) has recently proposed the following model for a typical section of a coal molecule:

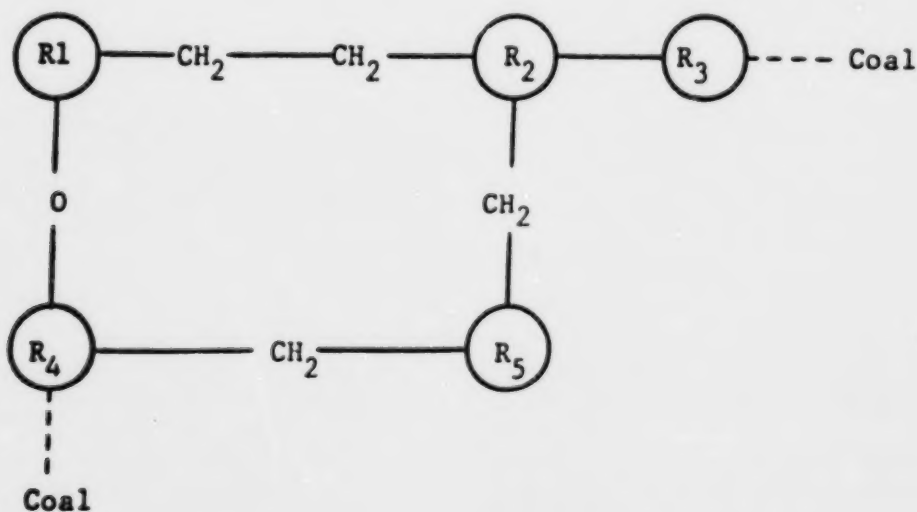


Figure 1: Proposed Model for a Section of Coal Molecule.

Where R_1 to R_5 are clusters of several aromatic, hydroaromatic and heterocyclic rings, some of which carry a phenolic hydroxy or a lower alkyl group; also oxygen bridges are present. The events taking place and the products formed during hydropyrolysis (without catalyst) of such a coal molecule were represented as follows (With adjustments to suit the purpose of this review):

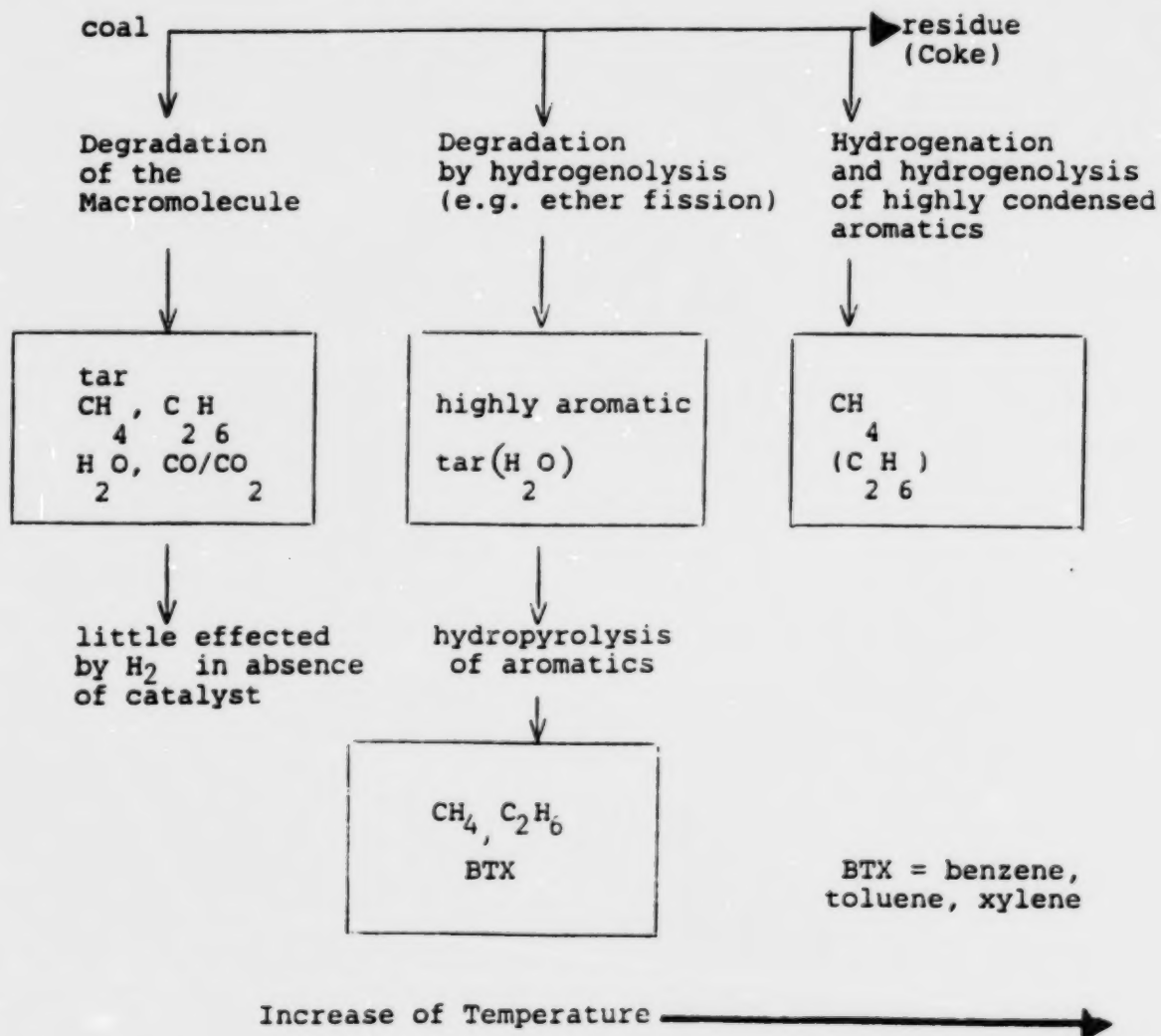


Figure 2: Chemical changes and products in hydropyrolysis of coal (without catalyst).

In the presence of catalyst hydrogen can participate in the degradation at lower temperatures.

The formation of aromatic tars from ethers in Figure 1 was depicted by the following (here simplified) reactions:

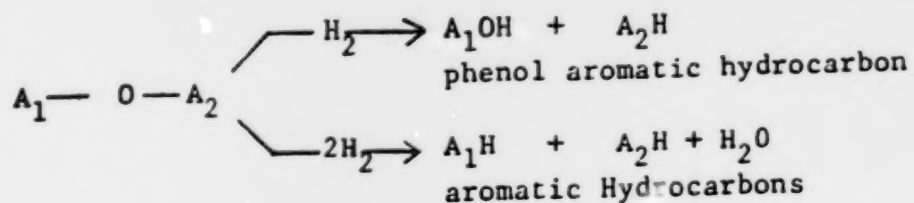


Figure 3: Formation of Aromatic tars from Ethers.

Where A_1 and A_2 stand for - probably condensed polynuclear - aryl groups, the formation of tars, i.e. of tri and tetracyclic condensed aromatics, from aromatics of higher molecular weight - partly formed by the above ether fission was presented by:

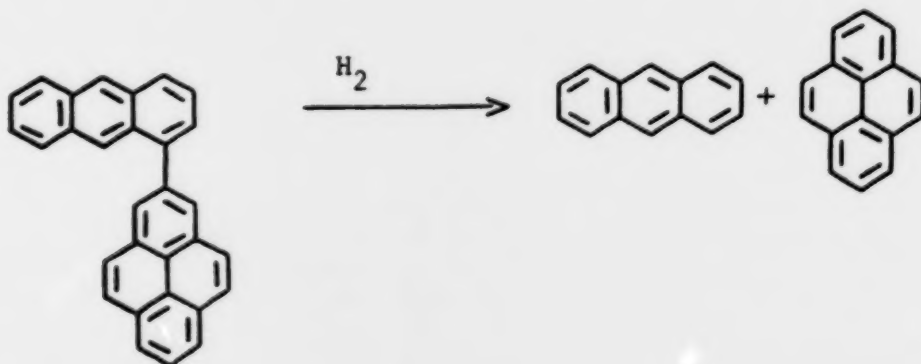


Figure 4: The formation of Tri and Tetracyclic condensed Rings.

The subsequent formation of the BTX fractions was shown to proceed via saturation of centrally located benzene rings and involved hydropyrolysis of hydroaromatic rings and of bisphenyl:

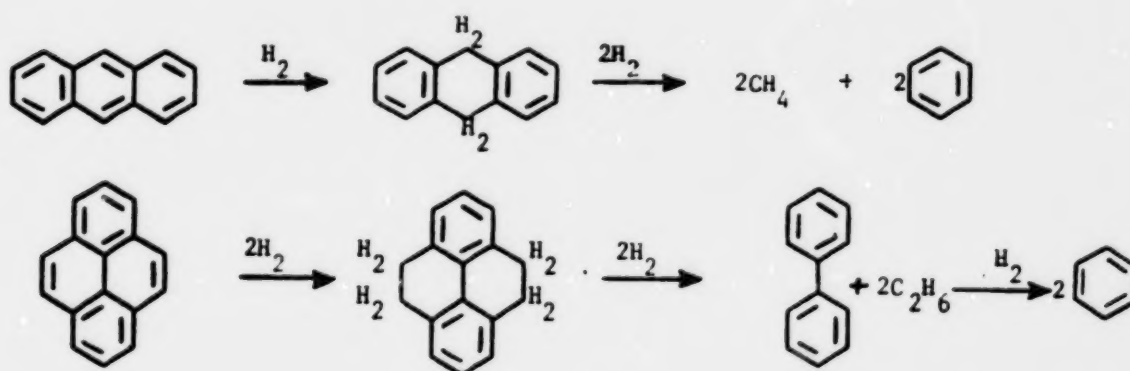


Figure 5: The formation of Products by Saturation of Central Rings.

Despite the presence of hydrogen - especially at lower pressures - some of the coal is being converted to more highly condensed polynuclear aromatics. Thus, via saturation of exposed aromatic rings and hydrogenolysis of the resulting hydroaromatic rings - the formation of lower alkanes, in particular methane, and polynuclear aromatic remaining in the reaction process can be explained.

In the recent work on the FHP of several condensed aromatic compounds, naphthalene, phenanthrene and chrysene,

R. N. Pandey (33) has proposed the following pathways from phenanthrene to the observed products as shown in Figure 6.

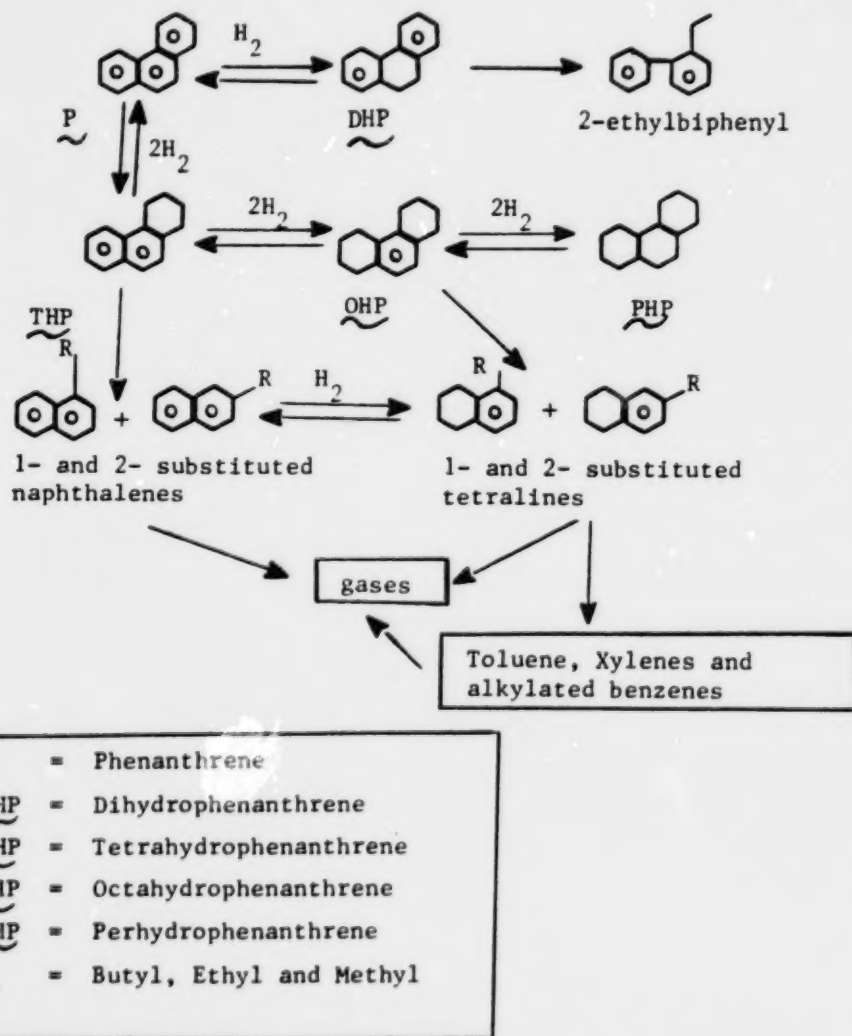


Figure 6: Proposed Pathways for the Formation of Products in FHP of Phenanthrene.

The demand for liquid fuels and starting materials has emphasized that a new technology for the conversion of high molecular weight materials must be developed. One such

technology is the application of flash hydrolysis to the substantial reserves of coal and residual high molecular weight materials. The technique is therefore considered to have far reaching economic implications.

This section reviews the research findings on the conversion of coal, residuum and related materials employing hydrolysis and flash hydrolysis, FHP. In doing so we have also examined and summarized experimental approaches, process conditions and results obtained as well as an outlook for the future.

Because the focus of this review is flash hydrolysis only appropriately selected hydrolysis processes have been included.

II.1 EXPERIMENTAL APPROACHES

A complete survey of the experimental methods used for the study of hydrogenation system is outside the scope of this review. Basically the following two methods have been commonly used.

II.1.1 Static Systems

The procedure followed in studying hydrogenation reactions has been to fill the reactor with known amounts of the reactants (or reaction mixture and hydrogenation catalyst) then raise the temperature and follow the reaction

products with time in a fixed volume at constant temperature and optimize the process conditions. Typical apparatus for studying such reaction is autoclave. Because of the convenience this method is by far the most popular and has been extensively used. A typical example is the recently studied batch scale hydrogenation of coal and coal model compounds, e.g. phenanthrene in the presence of in-situ hydrogen (produced by methanol decomposed over ZnO-CrO_2 catalyst) and hydrogenation catalyst, e.g. Ni, Co at 400-440 °C by Japanese researchers (3,4).

II.1.2 Flow Systems

One of the difficulties inherent in the conversion of bitumeneous high molecular weight materials is the complexity of the reacting system caused by secondary reactions which may follow the primary conversion/upgrading.

The conversion/upgrading of bitumen pitch or coal is based on the reaction of polynuclear aromatics in asphaltene and maltene fraction present in pitch with hydrogen at high temperature and pressure in the presence or absence of catalyst. The following reactions may take place:

- o Cracking of the asphaltenes and other heavy components into lighter compounds, resulting in a lowering of the molecular weight.
- o Hydrogenation of the resulting unsaturated hydrocarbons.
- o Elimination of heteroatoms, e.g. S, N, O as H_2S , NH_3 ,

H₂O.

- o Formation of gaseous hydrocarbons.
- o Polymerization of the unsaturated hydrocarbons and aromatics to form heavy polynuclear compounds and carbon.

The first three reactions above are desirable in the process study while the last two reactions are undesirable. A very popular method for studying the conversion is to allow to flow the reactants through the reactor for a period of time (residence time) which may be controlled. In this way, without permitting secondary reactions to become important, effect of reaction parameters e.g. temperature, pressure and catalyst is optimized to yield desirable products. It is this technique which has been used in the study of Flash Hydropyrolysis reactions.

II.1.3 Method of Rapid Heating

Flash Hydropyrolysis is considered to be an advanced experimental technique requiring rapid heating and quenching of products. A number of methods have been used for rapid heating: (1) laser, (2) microwave, (3) flash tube, (4) plasma, (5) electric arc, (6) shock tube, (7) electric current, and (8) entrained gases. R. J. Belt and L. A. Bissett (5) have reported the early development of these techniques and are included here for brevity and for the benefit of the general reader. Only the latter two techniques i.e. electric heaters and entrained gas heater

hydrogenation system which have current and future process applications will be presented in detail.

Lasers

While laser beams are efficient in producing extreme temperatures for short durations, the feed could not be heated uniformly over any significant area of the substances under study. In all laser studies, quantitation of conversion products other than the gaseous ones were not possible with any reliability. The effects of residence time, heating rate, carrier gas and particle size were not explored.

Microwaves

Microwaves have been used instead of electric arcs to generate plasmas for coal pyrolysis. A gaseous mixtures of H_2 , CH_4 , C_2H_2 , CO and CO_2 were produced with some evidence of liquids formed. As in laser studies, effect of process variables have not been reported.

Flash Tubes

Pyrolysis experiments with exposure time from micro to milliseconds have been carried out using a flash of high-intensity light as a source of heat. The ultra rapid heating of a thin film of small particle of coal was used. The results were similar to microwave studies. The use of filters to remove ultraviolet light from a xenon flash tube,

however, resulted in an increased yield of paraffins and olefins by a proportional decrease in the formation of CO , H_2 and acetylene (5). Detailed studies were not carried out.

Plasmas

Pulverized coal particles have been injected into a stream of high temperature gas plasma by preheating the gas through an electric arc. Temperatures as high as $15,000^\circ\text{C}$ have been achieved and acetylene comprised more than 15 per cent of the hydrocarbon produced (5). The yield of acetylene and hydrogen were higher with increase in temperature. It was further found that yield of acetylene could be enhanced by using small amounts of hydrogen in the argon stream.

Electric Arcs

In preliminary studies, pyrolysis of coal by high intensity electric arc between a cathode and an anode resulted in the formation of gaseous mixtures of C_2H_2 , C_2H_4 hydrocarbons, CO , CO_2 and H_2 . Liquid products were not detected.

Shock Tubes

A shock tube consisting of two sections, a high pressure gas driver section on one end, and a suspended coal particle-filled reactor section on the other separated by a diaphragm in between the two sections were used by E. F. Woodburn et al. (6) Upon bursting of the diaphragm, shock waves formed

by the gases rushing into the reactor section caused sudden increases in temperature (600° to $1,150^{\circ}$ K) in a fraction of a second due to the velocity disequilibrium between the solids and gases in contact. The results indicated a low yield of gaseous products and greater yield of unsaturated hydrocarbon as compared to conventional longer reaction times. Attempts to obtain kinetic parameters were not materialized in limited experimental studies.

Electric Current Heaters

Many researchers still apply original bureau of mines technique of using electric current for rapid heating of the feed sample. As mentioned earlier rapid heating is accomplished by passing high current at low voltage through heater/reactor. This type of heating allows bench scale studies to be carried out as a function of residence time, heating rate, final temperature, carrier gas pressure and particle size. The results have been encouraging in that the yield of low boiling is significantly enhanced by selecting appropriate condition.

Entraining Gas Heaters

The method entails feeding powdered charcoal vertically or horizontally into a heated reactor allowing charcoal either to fall freely through a heated zone or to be entrained by a preheated gas through a reaction zone.

Temperature in the reactor is maintained by preheating the entraining gas and/or externally heating the reactor. Pilot plant scale studies of pyrolysis and hydropyrolysis using entraining gas reactors are now commonly employed in a number of studies to be discussed later in this review.

II.2 Early Work

While the hydrogenation of coal has been in laboratory practice for nearly a century, the work of flash hydropyrolysis can be traced back to only decades. In 1914 Bergius obtained patents on the treatment of coal with hydrogen under pressure, at temperatures up to 500 °C (7). Subsequently coal liquefaction received commercial development in Germany, England and Japan. It can be argued that World Wars I and II would have been of shorter duration without such commercial realizations.

The pioneering work on hydrogenation under rapid heating and cooling of the coal appear to have begun by R. W. Hiteshue et al. (8) of US Bureau of Mines. A tubular flow reactor of stainless steel, type 304, having outside diameter 5/8 inch and inside 5/16 inch and 6-foot in length was used. The authors were capable of attaining a temperature of 800 °C in about 2 minutes and could cool the reactor to room temperature in about 10 seconds by spraying the entire assembly with cold water. This technique of attaining rapid

heating and cooling was considered to be a major breakthrough and differed from earlier conventional autoclave techniques of accomplishing the severity of reaction conditions which required longer heating and cooling cycles (3 to 4 hours). The rapid heating was attained by supplying a current up to 700 amperes at 9 volts. This preliminary work which began with the objective of studying the effect of short residence time on the conversion and distribution of gaseous and liquid hydrocabons from coal continued by Hiteshue group in their subsequent studies (9). The data on the analysis of yields of gaseous and liquid hydrocarbons are less reliable, mainly due to handling of small quantities - rather from a large system. Most certainly the data was satisfactory for studying the trends of the effect of temperature and residence time on yield and conversion. A plot of yield of liquid and gaseous product per unit conversion of coal with respect to temperature at zero residence time (~40 sec) is given in Figure 7.

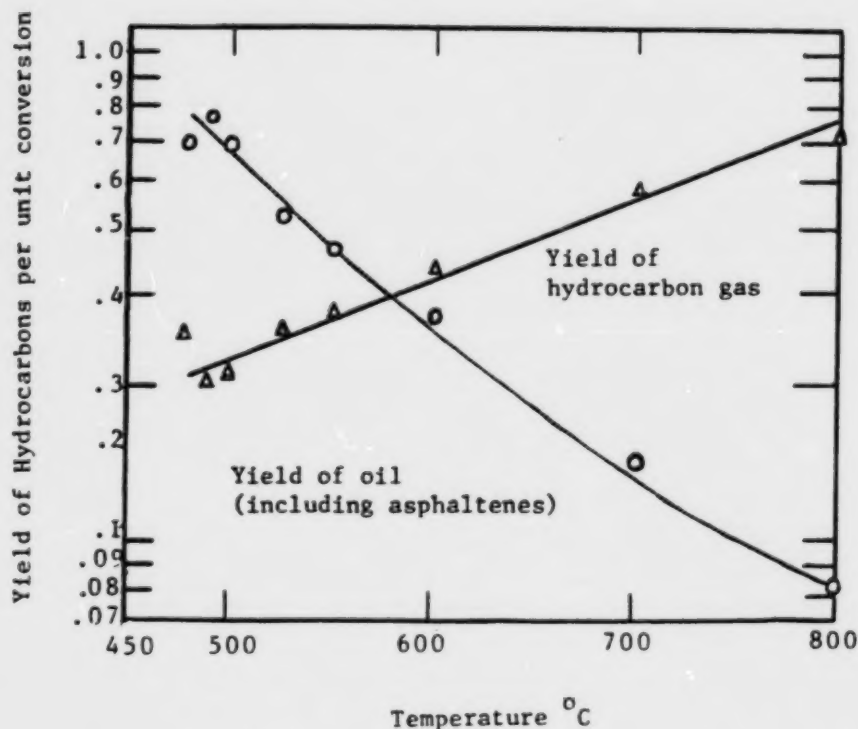


Figure 7: Yield of Hydrocarbons Per Unit Conversion, Zero Residence Time (9).

The remarkable feature of this study at zero residence time was that the yield of oil decreased with temperature whereas the gaseous products increased. The intersection point at 575 °C represented equal yields of liquid and gaseous hydrocarbons. Furthermore without catalyst the maximum yield of oil was found between 525 °C to 600 °C, whereas with catalyst the maximum yield of oil was obtained at 500 °C. At lower temperature and without catalyst the conversion and yield of product were lower than those obtained with catalyst. However, at higher temperature (700-800 °C) the catalyst was found to have no effect on the conversion and yield implying

that the hydrogenation of coal above 700 °C were thermally controlled. Based on their studies of the formation of asphaltene in the product the authors (11) further suggested the use of two catalysts: one to convert coal to high molecular weight oils and the other to effect adequate hydrogenation of these primary products to low-boiling oils. These studies do not appear to have been followed up.

A number of new developments have followed since the pioneering work of Hiteshue and the research work continues on the aspects of the effect of heating rate, short residence time, pressure and temperature. Special emphasis has been placed on experimental approaches, and analytical procedure due to a broad range of product spectrums ranging from gases (C₁ to C₄), hydrocarbons, liquids with BTX contents and heavy tars. Despite the number of exploratory studies, mostly on coal, the reaction mechanisms and kinetics remain poorly understood as to-date. The historical development of these studies are discussed below:

M. J. Finn et al. (10) of the National Coal Board, U. K. studied the hydrolysis of British coals. In a 1830 mm long x 8 mm i.d. stainless steel pressure tube, a sample of coal was secured between degreased wire wool plugs and the tube was heated by passing a large electric current (up to 1600 amps.) through the wall. The pyrolysis vapours were

swept out of the reaction zone by pressurized hydrogen at up to 15 MPa (150 bar). While some of the liquid products were collected in ice-cold traps, the remaining liquids and gases were reduced to atmospheric pressure through a needle valve before being collected for analysis. The products in the traps were weighed and then washed from the trap and adjoining tubing with chloroform. The residual char in the reactor was weighed and analysed.

Both gaseous and liquid products were analyzed by gas chromatography. For a 10 second vapour residence time, the yields of BTX and phenol, cresols and exlenols (PCX) reached a maximum at 727 °C. The maximum yield of single-ring aromatics was approximately 4.5% being composed of an equivalent amount of BTX and PCX. At 10°, 20°, 30° C/second heating rates and 727 °C final temperature, the yield of BTX increased steadily over 2-12 second range of residence times. At 3 second residence time the PCX was almost completely destroyed after an 8 second residence time. Dehydroxylation of PCX to BTX at longer residence times only partly explained the disappearance of PCX.

An extension of the above work using a two-stage hydro^opyrolysis in which vapourization of coal at 427 °C followed by thermal cracking at 1000 °C resulted in higher yields of aromatics (10). An increase in H₂ gas pressure

resulted in increased yields of methane and ethane.

J. R. Kershaw et al. (11) of Fuel Research Institute of South Africa studied the hydropyrolysis of coal using stannous chloride as a catalyst. The coal impregnated with the catalyst (stannous chloride solution in water was mixed with coal and the resultant slurry was dried over N_2) was mixed with sand and was held within the heater/reactor with steel wool plugs. The reactor was heated by direct resistance heating at a rate of $200\text{ }^{\circ}\text{C}/\text{minute}$. The vapour was swept away with H_2 gas at a flow rate of 22 L/min. and a pressure of 25 MPa.

The oils were trapped and subsequently fractionated by adsorption chromatography on silica gel by successive elution with petroleum ether, toluene, chloroform and methanol (11). The most significant finding of the study was the effect of catalyst on the product composition. Although an increase in the catalyst concentration in the range 1 to 10% reduced the heteroatom content and viscosity of the oil produced, there was no mention of an increase in the yield. An increase in reaction time and solid residence time resulted in increased yields of lighter oil fractions of low molecular weights and aromatics. Increasing the reactor temperature had both positive and negative effects on the quality of oil.

W. B. Russel and D. A. Seville (82) of Princeton University, New Jersey studied flash hydrolysis of coal using a captive cell reactor in which small sample of coal was spread evenly within a folded piece of stainless steel wire mesh and sealed in a pressure vessel. The sample was then subjected to a temperature program by heating the support electrically. Heat up rate was maintained at 10³ °C/sec. The fractional yield was determined solely from the loss of weight of coal sample after pyrolysis. The reactor was quenched in less than 0.1 sec. by spraying the cell with cold nitrogen. At about 580 °C, the yield increased slowly from 20% at 4 seconds to 24% at 8 seconds before stabilizing at 29% after 30 seconds. The weight loss became constant at 700 °C with a maximum reached between 550 - 580 °C. In general, the results indicated that the rate of pyrolysis is a sensitive function of reaction temperature, fast heating rate, pressure and particle size. The gaseous and liquid product distribution as a function of reaction variables was not studied.

P. C. Stangeby and P. L. Sears et al (12,13) employed an electric current type heaters to study the hydrogenolysis of coal and biomass samples. Preliminary studies indicated that the heating rate has significant effect on product yields. The effect of hydrogen gas was not studied over wide pressure range. However, it was noted that the heating rate and final

temperature as well as H_2 pressure significantly affected product yields.

Rockwell International Energy Systems Group, California (14) undertook a study of hydrogasification utilizing entrained flow reactor testing of peat dense-phase feed system. Without the use of any catalyst, the hydrogasification reactor testing was performed at peat throughput rates of over 455 kg/hr 1000 (Lb/hr) and reactor temperatures to 1038 °C (1900 °F) in hydrogen atmospheres from 3.4 MPa (500 psig) to 0.7 MPa (100 psig). A flow diagram of the reactor is shown in figure 8.

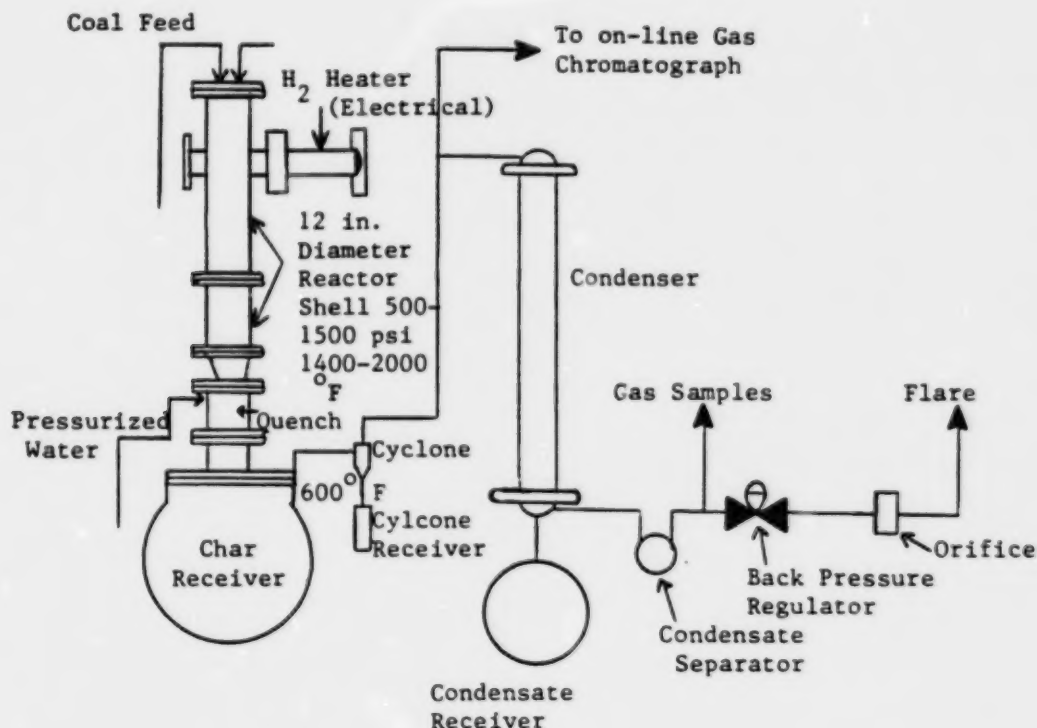


Figure 8: Simplified Flow Diagram of Rockwell 3/4-TPH Reactor System

On-line gas chromatographs in conjunction with product gas traps located just downstream of the char cyclone were used to determine the product distribution and composition. The results indicated that increasing the reaction temperature, hydrogen partial pressure, and residence time led to increased conversion efficiencies; as high as 85% carbon conversion was claimed. For moderate residence times of 1-4 seconds, the BTX formation was optimal between 870 - 925 °C reactor temperatures. An increase in hydrogen pressure

decreased the BTX yield. Heavy oils did not appear as products at reactor temperatures above 925 °C (1700 °F) for residence times greater than 1 second, thus suggesting thermal cracking of high boiling fractions. The high temperature thermal cracking was found to be independent of hydrogen partial pressure.

Cities Service Research and Development Company in Oklahoma (15) carried out flash hydrolysis of bituminous coal with catalysts. A vertical stainless steel reactor tube (5 ft. long x 3.1 inches i.d.) was fitted with a stainless steel injection tube on the top of the reactor for feeding coal by pressurized carrier gas. Preheated hydrogen entered the reactor from a tube located at the side of the reactor. The char, reaction products and unreacted hydrogen were allowed to pass through the reactor in a free fall mode. Thermocouples, located throughout the reactor, measured the gas stream temperatures. A three-zone electrically heated furnace surrounding the reactor was used to control the heat losses from the wall of the reactors.

Three chilled liquid condensers were used in series to collect the product gases passing the char pot. The condenser off-gases were further trapped of hydrocarbon vapours in an activated carbon trap. The carbon trap adsorbed the heavier hydrocarbons in the gas, mainly BTX.

Condenser off-gases were sampled and analyzed by gas chromatographic technique.

Catalysts were added to the coal by dissolving the catalyst in distilled water, and then adding the solution to the coal, homogenising, drying, and crushing to pass 50-mesh screen. Catalysts used included chlorides and sulfides of Ni, Zn, Cu and Fe, of which only zinc chloride was effective (>80% carbon converted) at 480 °C (900 °F), but not above 650 °C (1200 °F). Nickel chloride, was the next best catalyst, but the yield was substantially lower ~ 25% as effective as zinc chloride.

Studies of parametric effects on product yields were carried out in the absence of catalysts. The results are summarized in Figure 9. Carbon conversion to liquid products peaked to 28 percent at 700 °C (1300 °F), while the light oil yield peaked to 18 percent at 750 °C (1375 °F) and the BTX yield maximum was 13 percent at 815 °C (1500 °F); all indicating sequential thermal cracking from coal to asphaltenes to oils to BTX and ultimately to methane. The hydrogen was considered to be acting to stabilize products and inhibit condensation reactions. The solid residence time was found to enhance the conversions at a reactor temperature of 480 °C (900 °F). Increasing the vapour residence time decreased the selectivity of the liquid products. A

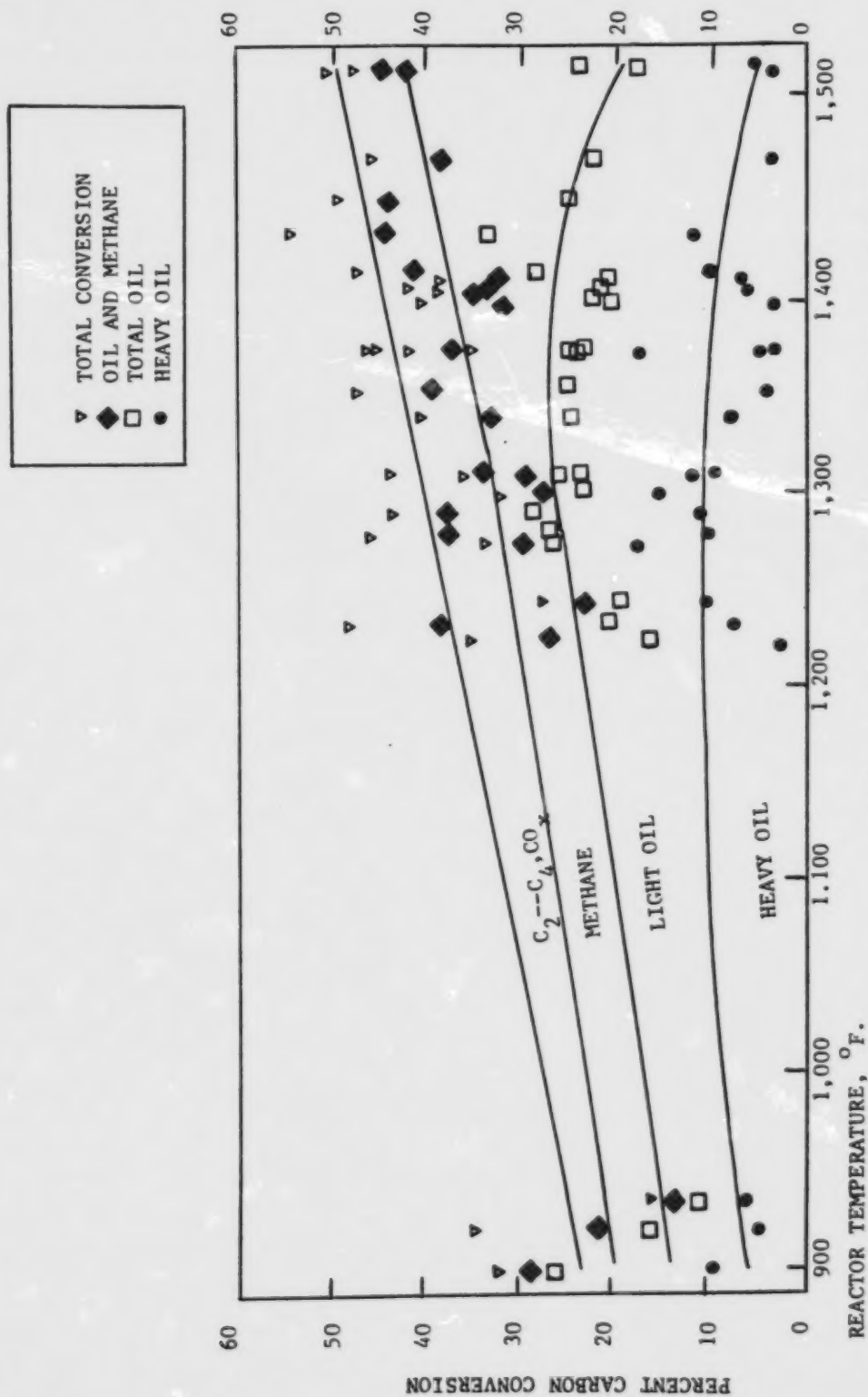


FIGURE 9 : EFFECT OF REACTOR TEMPERATURE ON PRODUCT DISTRIBUTION WKB COAL

residence time greater than 10 seconds allowed more hydrocracking than shorter resident time and more gases were produced. The observed data were too random to conclude any definite effect of vapour residence time on the formation of BTX.

Flash pyrolysis of coal with reactive and non-reactive gases was carried out by M. Steinberg et al. (16) at Brookhaven National Laboratory, Upton, N.Y. The reactive gases were H_2 , CH_4 , CO and CO_2 whereas non-reactive gases included He, N_2 and Ar. As shown in Figure 10, an 8 foot long and 1 inch i.d. entrained downflow tubular reactor system was used.

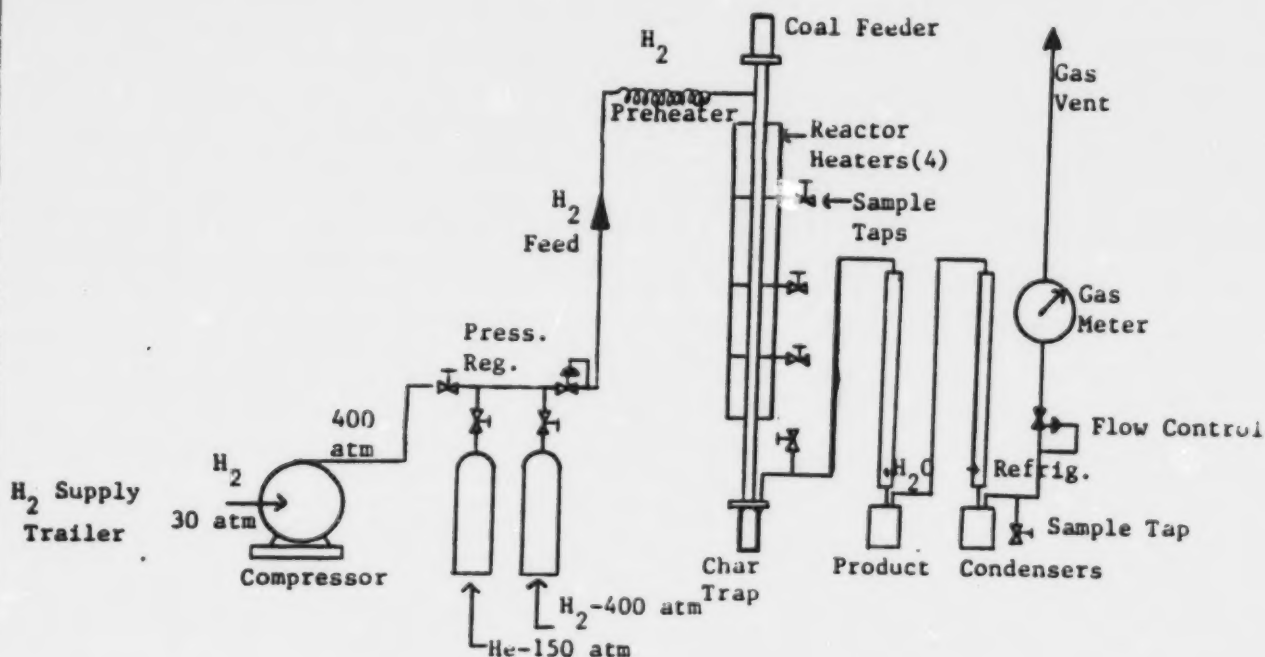


Figure 10: Schematic Flowsheet of Entrained Tubular Reactor Experiment. (16)

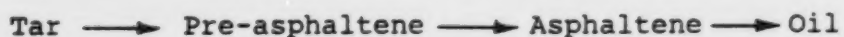
Coal particles 150 microns or less in diameter were fed by gravity. The gas being used were preheated and contracted coal particles while passing through the reactor. The heat transfer, pyrolysis and secondary reactions were allowed to take place as the coal and entraining gases concurrently moved downwards. Product laden gases were cooled to 250 °C by a forced air cooling. The char was removed from the effluent gas in a high pressure vessel at the bottom and the effluent gases passed through -15 ° and -40 °C condensers in series.

The condensibles were vented to the atmosphere. Coal feed rates were about 500 g/hr. On-line GC was used to determine CO , CO_2 , CH_4 , C_2H_4 , C_2H_6 , BTX and low boiling components every 8 minutes. Products heavier than BTX ($>\text{C}_9$) could not be analyzed by gas chromatography. These products were extracted in solvent, solvent removed and the product weighed. The quality of heavy liquids produced were examined by I. R. Spectroscopy to detect classes of organic compounds present but data was found too complex to interpret.

Material balances on carbon averaged at 80% of coal fed for nitrogen carrier gas and the carbon monoxide yield was estimated at about 5%; the remaining 15% material balance on carbon remained unaccounted for. In the presence of hydrogen as carrier gas the material balance on carbon averaged for about 96%. The carbon balances for experiments with methane gas were poor (about 78% on average due to lack of analytical accuracy in determining methane in the feed).

Attempts were made to characterize the composition of tars produced on the basis of solubility in benzene, and hexane. The results indicated that pre-asphaltenes (benzene insoluble) was only a very small part of the tar. When the pyrolysis gas was methane, an increase in tar yield was accompanied by an increase in oil yield. The authors

suggested following reaction sequence in the flash hydropyrolysis experiments:



The flash pyrolysis of New Mexico sub-bituminous coal, both in reactive and non-reactive gaseous environments, was very rapid under the conditions investigated (20 to 500 psi and 800° to 1000° C).

The total carbon conversion followed the order: $\text{H}_2 > \text{CH}_4 > \text{CO}$. In case of non-reactive gases such as helium, the tar yield tends to increase with increasing pressure as expected in hydrogen deficient atmosphere. Benson et al. (17) utilized a bench scale 1/8" i.d. x 70' long helical tube down-flow entrained gas reactor. The lignite and bituminous coal feed was flash hydropyrolyzed inside the reactor to 815° C (1500° F). The effluent passed into the char trap where the spent char was disentrained and collected, while the char-free gases were further cooled to ambient temperature to condense liquid products which were collected in sample bombs. The cooled gases were reduced to atmospheric pressure, and passed through a dryer and methanol/dry ice freeze-out train to strip benzene and other condensable materials from the effluent gases, which were sampled and vented. The results indicated that the conversion of oxygenation lignites to BTX and alkyl benzene are dependent

on the heating rates up to 65 °C/sec (150 °F/sec) at about 800 °C final temperature as well as the hydrogen gas pressure up to 13.78 MPa (2000 psig). The distribution of feed carbon among the products was found to be independent of the heating rates higher than 150 °F.

D. S. Scott et al. (18) has designed and operated a stainless steel fluidized bed continuous flash pyrolysis reactor for flash pyrolysis of finely particulate (-30 mesh) biomass materials. Fluidized gas throughout rate was maintained in the 400-650 mL/min range. Typical runs at variable temperature and a constant vapour residence time of 0.44 seconds indicated that tar and organic liquid yields peaked at about 500 °C under atmospheric pressure conditions for aspen-poplar sawdust and the total organic liquid approaching 65% of the dry wood fed.

II.3 Recent and Current R & D Trends

A. General Comment

Significant advances made in aspect of the research entailing the reactor design, analytical techniques, catalytic effects and, kinetics and mechanistic interpretation of the results are now presented. While a chronological anecdote of all research and development activities is beyond the scope of this review, attempt has nonetheless been made to assimilate the vast information and

highlight those aspects which are expected to contribute towards further research efforts. In doing so we may have treated lightly certain topics or ignored in the hope that it has been fully presented elsewhere.

While coking processes have long been established (19,20) as the principal means of producing liquid fuel and metallurgical coke, residue thermal hydro-cracking has gained considerable importance in the recent past (21,22). Earlier research discussed in the previous section, clearly demonstrated that hydropyrolysis (HP) is more amenable to yielding higher proportion of liquid products when compared to pyrolysis in an inert atmosphere. In addition, processing of coal, coal-tar and pitch by HP produces char, which can be used as feed to the coal fired electric generators (19,20). The chars from HP process are generally free from sulphur and nitrogen - containing impurities and their use in boilers is considered to minimize the environmental impacts of gaseous emissions (19,20). Figure 11 is a generalized process flow diagram for pyrolysis/hydropyrolysis of coal.

It should be pointed out that pitches and coal-tars are somewhat analogous to tar sands in so far as their asphaltene contents are concerned (23,24,25). As the conventional crude oil reserves are depleted, efficient utilization of coal-tars, pitches and tar-sands will play an important role in

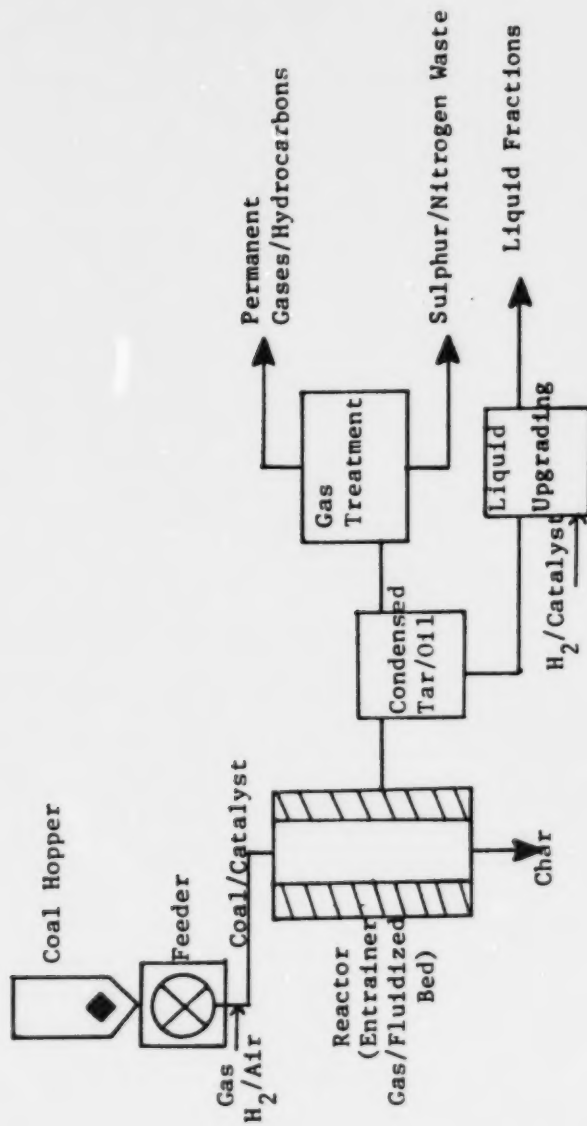


FIGURE 11: Generalized Process Flow Diagram for Coal Pyrolysis/Hydrolysis.

meeting the long-term energy needs (20). Current research efforts are therefore directed not only towards finding efficient means of converting coal into liquid fuel, but also to converting the vacuum residues of a wide variety of feedstocks such as tarsand bitumen and pitch into cracked oil with maximum liquid product yields (22,26,27).

B. Current Reactor System

Currently Brookhaven National Laboratory, Upton, N.Y. uses a bench scale downflow entrained bed tubular reactor (28,29), 8' long and 1" i.d. (1.5" x 0.25" Inconel 617 tubing) having a 30 g/min. coal flow and 150 g/min hydrogen flow capacity at 1000 °C temperature and 27.56 MPa (4000 psig) pressure over a 2-hour semi-batch operating period. A schematic flow diagram of the process equipment is as shown in Figure 12.

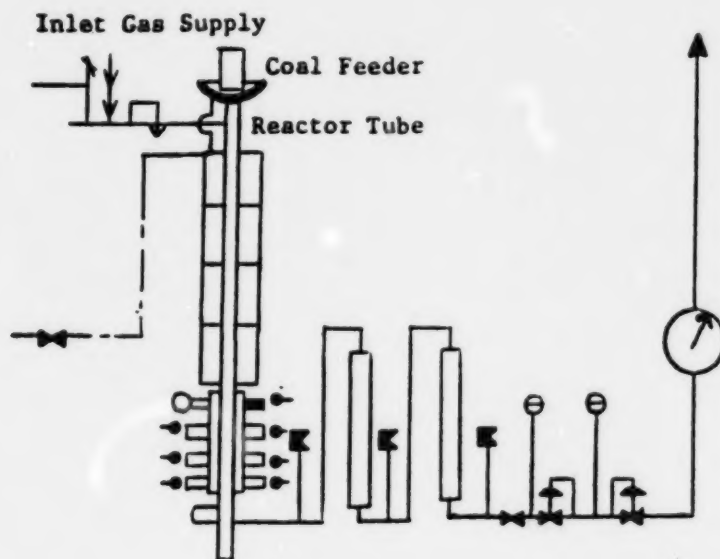


Figure 12: Recent Coal Flash
Hydropyrolysis system (29).

The reactor is heated by four 2' clamshell type heaters of 2300 watts each, and the cooling section contains eight blowers to be used as necessary to cool the product gases to less than 400^o C. Sample traps are provided at 2' intervals along the length of the reactor to allow sampling for residence time, product distribution and yield determination. The results of the bench-scale studies with this reactor will permit their application to fluidized bed reactor (FBR), concurrent downflow entrained bed (EBR) and fast fluidized bed (FFB) reactor design concepts. The basic design considerations are discussed in reference 28.

Suzuki et al. (30) have designed a two stage quartz reactor tube, 300 mm long, 18 mm i.d. at lower section and 8 mm at the upper section. The reactor is placed vertically in an electric furnace. The lower and upper ends are heated independently by adjusting electric current to the heaters. Heavy oil samples were fed from a micro-feeder through a hypodermic needle to the top of the inner tube located in the lower section of the reactor. The pyrolyzed oil was carried to the upper section by argon flow for the second stage of pyrolysis at a different temperature. Residence time at the second stage was controlled by changing the argon flow rate/ Although the reactor design allowed small scale pyrolysis under atmospheric pressure, it is limited by its application to liquid fuels only.

R. N. Pandey (31) has designed and assembled a single-stage electric current type pressurized reactor unit consisting of a 0.25" i.d. x 15" long 304 stainless steel tube having a wall thickness of 0.035". A schematic diagram of the reactor is shown in Figure 13.

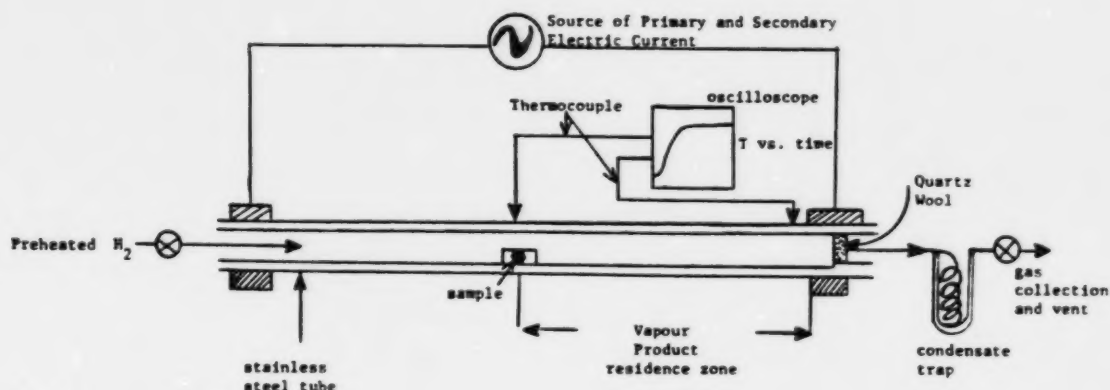


Figure 13: Schematic Diagram of Reactor Heating, Residence Zone and Temperature Measurement.

The reactor system allows step wise temperature increases to 1000 °C in 1 to 2 seconds. A type K thermocouple spot welded to the reactor tube was used in previous studies to record the temperature by means of linearized digital thermometer. The temperature measurement in current studies is now made by the use of oscilloscope. A switching control unit consisting of a series of solenoids actuated by two timers have been used to control the heating circuit from a bank of heavy duty batteries.

W. H. Calkins et al. have designed and operated a bench scale fluidized bed pyrolyzer (32,33). The coal particles entrained in a nitrogen stream, were injected into a sand bed fluidized with nitrogen and heated in a split furnace to

850 °C temperature and a contact time of 0.5-1.0 sec achieving heating rates of the order of 10^4 °C/sec. Volatiles emitted from the coal were passed through two cold traps in series containing cellulose Soxhlet thimbles to filter the tar and char allowing gases to be monitored by GC.

D. E. Walsh and N. Chen (34) designed and operated an electric heater type reactor. Their reactor is schematically shown in figure 14.

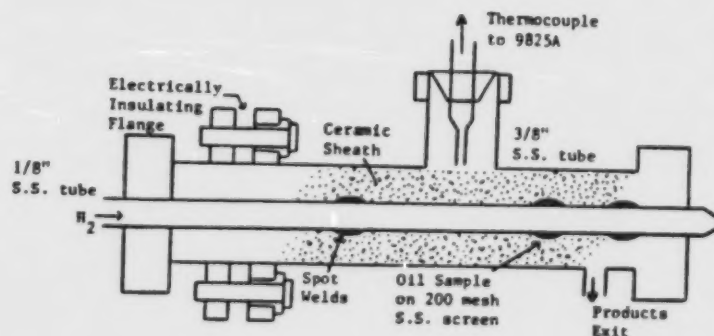


Figure 14: Flash Pyrolysis Reactor schematic (34).

Heating rates up to 800 °C/sec was achieved by an electrical switching relay circuit.

A conceptual design of a plug-flow tubular reactor having special vertical feeding, rapid heating and cooling devices has been proposed (35). The design characteristic of the reactor will allow ultraflash pyrolysis of coal, wood, and other solid feed materials in continuous operation.

C. Analytical Method

The efficient analysis of pyrolysis products of coal, coal-tar and petroleum residues is as challenging as the pyrolysis process itself. This is clearly evident from the various analytical tools and techniques employed by researchers. Classical methods (34,37) of fractionating liquid streams from the reactor are schematically shown in figure 15.

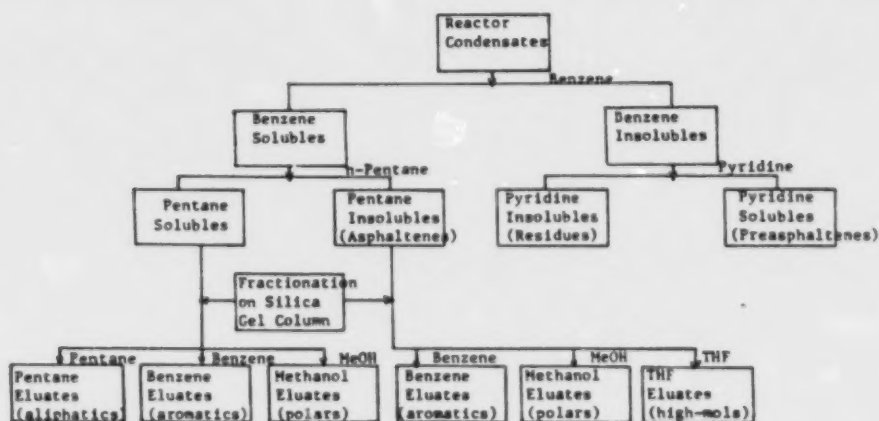


Figure 15: Fractionation Scheme for Reactor Condensates (34,37).

The benzene-soluble portion is called "oil", whereas the benzene-insolubles are called "asphaltenes". Part of the "benzene-insolubles" soluble in pyridine, "reacted coal" or "preasphaltenes" are characterized by their high viscosity. The pyridine insolubles are regarded as the unreacted coal or residues. The benzene-soluble fractions are of primary importance in characterizing the efficiency of a pyrolysis

process.

It can be seen that no single analytical tool will accomplish complete identification and quantification of the benzene soluble fraction of interest. Under plant-scale processing conditions (15) reactor fluid streams were condensed in up to three condensers at different temperatures to fractionate the liquids with the heaviest fraction condensing first. The effluent from the traps containing BTX fractions were further collected in activated charcoal traps before releasing the gases to be monitored by an on-line GC. When under process conditions, activated charcoal traps were not in use, BTX were reported to be condensed in flow system downstream from the condensers (14) and therefore BTX components could not be measured quantitatively in the on-line GC.

Although pyrolysis gas chromatography (PGC) is widely used, various inadequacies have been reported (36,38). These include the nonspecificity of GC separation to individual classes of hydrocarbons (aliphatics, aromatics, polar materials, etc.) due to the elution on GC column mostly by boiling point of individual components. In addition, there are no single or dual detector system universally applicable to simultaneously distinguishing hydrocarbons from nitrogen or sulphur containing heterocycles with high sensitivity,

resolution, reproducibility and fast analysis time (39). To overcome these difficulties, GC analyses have in many instances been supplemented by mass spectroscopic analyses of GC fractions. It should be noted, however, that MS analyses become cost effective only when a GC fractionation pattern has emerged and requires specific information with regard to confirming the identity of various fractions not amenable to retention time calibration by normal GC techniques (38). Furthermore, GC technique require high temperature profile of elution thus temperature may cause decomposition of some of the labile fractions. Also the destructive detection devices employed in GC, do not permit collection of fractions for further structural analyses.

W. H. Calkins and R. J. Tyler (32) in their studies of coal flash pyrolysis utilized preparative high pressure liquid chromatography (HPLC) to isolate and purify polymethylene chains believed to be precursors to olefins in the pyrolysis of coal. This was achieved by successive isocratic elution of a fraction of tar sample on a silica gel column using various solvent systems. The isolated fractions were further analyzed by infrared and nuclear magnetic resonance spectroscopic techniques.

M. L. Selucky et al. (38) utilized HPLC to analyze petroleum and petroleum derived products on micro-porasil

columns equipped with U.V. and Refractive Index (R.I.) detectors. The chromatograms successfully separated hydrocarbons from polar materials, particularly saturated aliphatics from aromatics. The use of a UV detector provided high sensitivity to mono, di and tri aromatics, while the use of R. I. detector afforded detection of alkanes. Except for some C₆ and C₇ isomers, when n-heptane was used as a mobile phase, hydrocarbons boiling lower than C₆ having lower refractive index than heptane has been indicated by a negative peak, whereas those above C₇ are indicated by a positive peak. The HPLC analyses in conjunction with GC afforded an excellent means of fingerprinting petroleum fractions from light virgin naphtha to lube oils, heavy crudes and heavy crude pyrolysis products. More specifically, the HPLC method allows non-destructive trace analyses of mixtures of alkyl benzenes, alkyl polynuclear aromatics and polynuclear aromatic hydrocarbons. Researchers in developing HPLC analytical methods (40,41) indicated that rapid analysis of components of heavy oil fractions is possible using both normal and reversed phase liquid chromatographic techniques, (42,44) depending upon the nature of sample used and the degree of separation desired. An important application of HPLC methods lies in determining the extent of heteroaromatic component present in the feed and the pyrolysate, which may indicate the nature of chemical

reactions applicable to transforming these heterocyclic compounds during pyrolysis processes.

Heavy oil fractions have also been subjected to ^{13}C NMR, PMR and Infra-Red spectroscopic analyses to obtain general information with respect to the nature and degree of unsaturation in hydrocarbons, (11) the methylene chains and hydroxyl radicals (11,32) of pyrolysis reactor feeds and liquid products. X-ray diffraction techniques and electron spin resonance spectroscopy have also been applied to investigate macrostructure of asphaltenes, (44) which are believed to be organometallic compounds of complex structures.

II.4 Results and Discussion

II.4.1 Effect of Key Parameters

Based upon the earlier exploratory research discussed in the preceeding section, two types of basic process design concepts have emerged in the current research and development program. These are: (a) electric current type reactors and (b) entrained gas reactors. With minor modifications in each case, the electric current type reactors have primarily been used to obtain basic data from bench-scale studies. The results from these carefully controlled experimental studies offer the primary physico-chemical data necessary to understand the chemistry of the pyrolysis processes in terms

of the key parameters, namely the effect of heating rate, final temperature, pressure and residence time affecting the kinetics and mechanisms of FHP reactions. The entrained gas type reactors on the other hand employs bench-scale as well as pilot plant scale flow through (continuous or batch-type) operations to optimize the above process parameters for maximum liquid product yields. Both methods are most certainly complementary to each other as far as their application to the future design and operation of plant processes are concerned. A brief discussion of the recent studies utilizing these two types of processes are given below:

Bunger et al. (25,45,47) have conducted a number of pyrolysis studies for potential upgrading of tar and bitumens. Utilizing semi-batch downflow entraining gas type as well as electric current tubular reactors, it has been shown that tar sand bitumens can be quantitatively converted into gases and medium volatility liquids with low hydrogen gas consumptions. The gas to liquid ratios increase with increasing temperature, and decrease with decreasing residence times. A hydrogen gas pressure above 8.26 MPa (1200 psig) has been found to inhibit coke formation. The optimum conditions to obtain the desired yields and to prevent extensive coke formation depend on the feedstock properties and compositions (47). It has also been shown

that heterogeneous catalysts are not required in the hydropyrolysis of bitumens. Elemental analysis, ^{13}C NMR, PMR, IR and gas chromatographic techniques have been used to assay the feedstocks and pyrolysis products to obtain evidences in support of free radical reaction mechanisms believed to be operative during the pyrolysis processes. It has been demonstrated that hydropyrolysis inhibits olefin production and the products are therefore expected to be more stable than those from coke distillates.

Pruden et al. carried out thermal hydrocracking of Athabasca bitumen (48,49) utilizing a vertical reactor in which the feedstock and hydrogen gas were fed at the bottom and the product liquids and gases were collected from the top. The pilot plant reactor in principle similar to an electric current type reactor, operated between the ranges of temperature and pressure of 410°C - 470°C and 13.79 - 24.13 MPa (2000-3500 psig) respectively. Higher temperature and pressure conditions increased the lighter product yields with decreased overall sulphur content. The quality and yield of gaseous and liquid products were found to be independent of purtiy of the recycled hydrogen gas.

Jayakar et al. thermally cracked tar sand (5) in an inert atmosphere between 450°C - 500°C temperature using a fluidized bed entraining gas reactor. Combustion of the

pyrolytic residue from the reactor at $550^{\circ} - 650^{\circ} \text{C}$ generated sufficient heat to allow preheating and pyrolysis of tarsands in the fluidized bed reactor.

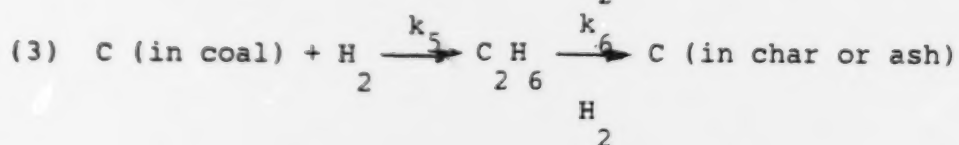
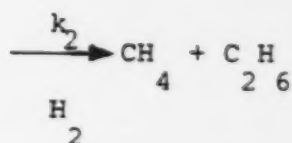
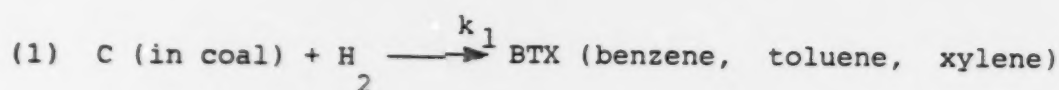
Fluid Catalytic Cracking (FCC) of heavy oils/bitumen was carried out using a two-stage pyrolysis technique by T. Suzuki et al. (30,51). The residual heavy oil was first thermally cracked at 440°C and the products were then carried to the second stage reactor at $750^{\circ} - 800^{\circ} \text{C}$ by argon flow. The second stage of pyrolysis was carried out over silica-alumina bed as a catalyst. The results indicated that long paraffinic straight chain hydrocarbon yields are abundant in oil from vacuum residues, whereas branched or alicyclic hydrocarbons are rich in the products from Cold Lake bitumen. Pyrolysis of all types of feedstocks used by the method produced olefins in significant yields.

In the pyrolysis and hydropyrolysis experiments discussed above, the residence time of volatized vapour has been measured as a function of carrier gas flow. Heating rates have not always been determined experimentally, but estimated to be in the range varying between 20°C/sec to $10^6^{\circ} \text{C/sec}$. Flash heating of Athabasca bitumen under carefully controlled heating rates up to $20,000^{\circ} \text{C/sec}$ for 20 sec at atmospheric pressure under isothermal conditions (52) resulted in thermal volatilization at temperatures up to

about 500 °C, followed by pyrolysis predominately at 950 °C. The initial volatilization step is dominated by the maltene fraction, whereas the asphaltene fraction undergoes degradation above 500 °C. In Flash pyrolysis/hydropyrolysis techniques, rapid rate of heating, and final isothermal reaction temperature are additional variables which allow control of the volatilization and pyrolytic processes.

Current flash hydropyrolysis/pyrolysis research (28,29) at the Brookhaven National Laboratory continues as a follow-up of the earlier studies. Utilizing a downflow entrained tubular reactor, fine coal particles (100 mesh) were allowed to flow through the reactor at throughput rates from 0.1 to 4 lb/hr. The gas and light oil product compositions were continuously monitored in an on-line GC and the heavier liquids, tars and chars were collected for analyses. Complete conversion of coal particles was achieved at solid residence time of about 4 seconds resulting in the formation of polynuclear aromatic hydrocarbons in the liquid fractions in predominant amounts. The effect of parametric change provided optimum product yields as a function of solid residence time, vapour residence time, heating rate, temperature, pressure, particle size, H/C feed ratio and catalysts (ferric oxalate and sodium carbonate).

Because of the chemistry and the complexity of coal structures the analysis of the modeling of the kinetics of coal hydrogenation reaction was found difficult. A simple two step consecutive reactions of carbon with hydrogen were assumed in separate reaction scheme to describe the kinetics of the hydropyrolysis process as follows:



Reaction (1) shows that benzene, toluene and xylene (BTX) in coal are devolatilized upon heating in the presence of hydrogen. BTX then decomposes or reacts with H_2 to form methane, ethane and char. Reactions (2) and (3) are the hydrogenation of coal to form methane and ethane which are then decomposed to form char. k_1 to k_6 are the rate constants of the reactions and are functions of temperature, pressure and other parameters. This three-step sequence,

which is certainly not the complete reaction chemistry, was the basis for predicting multi-component yield behavior. The model did not include the intermediate formation of volatile free radical hydrocarbons (e.g. $\text{CH}_2^\bullet$, $\text{C}_2\text{H}_5^\bullet$ etc.) which are usually postulated in the detailed reaction mechanisms.

The above model scheme was subjected to regression analysis to obtain the best fit of data under various parametric changes of the process conditions. Good correlation was obtained between the yield predicted by the kinetic model and yield actually observed. Although the results allow no simple interpretation in terms of any meaningful reaction mechanisms operative at the molecular level, an estimated activation energy of the order of 20 kcal/mole implies that the rate-determining step is some sort of a chemical reaction which may involve the formation of free radicals.

Using an electric current type reactor, W. Chen et al. (53) have studied flash hydrolysis of U.S. coals. Under conditions of $650^\circ\text{C}/\text{sec}$ heating rates to 800°C temperature for a 10 second contact time and 0.6 sec vapour residence time under a hydrogen pressure of 101.3 MPa, the various types of coals were subjected to routine studies to characterize them by total liquid yields. The methane, ethane and BTX from the FHP of coal were 5 to 10 times higher

from pyrolysis under similar conditions. The significant observation was that the total carbon conversion decreased with increasing rank from lignite to high volatile bituminous coal, whereas the total liquid yield (which includes BTX and heavier liquids) increased with increasing rank of coal.

A. J. Koplick et al. (54) studied the properties of asphaltenes derived from tar from the flash pyrolysis of Australian coals. The asphaltenes were first separated into acid, base, polyfunctional and neutral fractions by ion exchange chromatography. Each fraction was then subjected to high pressure hydrogenolysis at 400 °C temperature, 13.8 MPa pressure and 1L/min. hydrogen carrier gas flow. GC-MS analysis of the volatile products revealed that most of the asphaltenes were composed of small one or two ring aromatic units with alkyl chains from C₆ to C₃₂ (with a maximum at C₁₆ - C₁₈).

W. H. Calkins and R. J. Tyler studied (32) the properties of tars obtained from flash pyrolysis of various coal particles (less than 200 micrometer) in a reactor bed of sand fluidized by N₂ at heating rates of 10 °C/sec to 700 - 800 °C temperatures and vapour residence times of 0.5 to 7 seconds. The tar fractions and tar vapours were analysed by 13 C-NMR, PMR, FT-IR, GC-MS and high pressure liquid chromatography (HPLC). Further pyrolysis of tars at 700 -

1100 °C (1-2 sec. vapour residence times) produced hydrocarbon products characteristic of those obtained on high temperature pyrolysis of coal itself, indicating that some of the olefin precursors in coal are transferred in some form to the tars. The tars contained long polymethylene chains ($C_{14}-C_{26}$, and higher) accounting for up to 35% of the product, the remainder consisted mainly of saturated and unsaturated aromatics.

R. N. Pandey (31) at Guelph Chemical Laboratories carried out flash hydropyrolysis of polynuclear aromatic hydrocarbons in the presence of Co-MO and Ni-W catalyst in the sulfided forms. Utilizing an electric current heater type reactor cell in the temperature range 600 °C - 900 °C temperature and 1.37-6.89 MPa (200-1000 psig) pressure, flash hydropyrolysis of naphthalene, phenanthrene and chrysene were carried out. The effects of catalyst to feed ratios and concentration of hydrogen on yields were followed. The gaseous and liquid products were analyzed by GC and GC-MS techniques. The use of catalysts resulted in 60-80% conversion of the polynuclear aromatic hydrocarbons. From the product distribution, it was noted that the yield of hydrogenation increased with increasing size of the feed molecules. A uniform heating rate of about 800 °C/sec was maintained throughout the experimental runs and vapour residence times of 1 and 2 seconds resulted in no significant

changes in product yields. The yield of hydrogenated product from Phenanthrene increased with increasing hydrogen pressure at about 750 °C and 2 second residence time. Identification and quantification of products provided valuable insights into the possible reaction pathways operable during hydropyrolysis of polynuclear aromatic hydrocarbons. These findings will be applicable to deducing conditions suitable for hydropyrolysis of asphaltene residues which are rich in polynuclear aromatic hydrocarbons.

II.4.2 Proposed Kinetics and Reaction Mechanisms

An understanding of the kinetics and reaction mechanisms of the transformation of coal, coal-tar and petroleum residues by pyrolytic and hydropyrolytic processes is beginning to emerge from recent research findings. While general trends of product yield and composition as a function of various reaction parameters provide some support for various speculated kinetic schemes discussed in previous sections, specific mechanistic interpretation of complex kinetic data from studies of model compounds form the basis for the proposal of mechanisms by which pyrolytic and hydropyrolytic (FHP) can be rationalized. It would therefore be prudent to begin with a discussion of some of the key studies using model compounds.

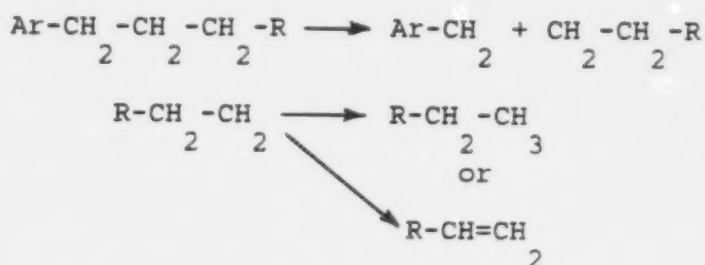
Rice and Herzfield were the first to propose in 1934 a general mechanism to account for an assumed first order kinetics of pyrolysis of butanes (55) and it is still generally agreed that uninhibited pyrolytic reactions proceed principally by a radical chain mechanism. In this mechanism:

- o Free radicals are initiated by the splitting of the molecule at its weakest link.
- o One of the radicals abstracts hydrogen from the parent molecule to form a small saturated molecule and a new free radical. Free radicals of the type $R-CH_2-CH_2$ can stabilize themselves by splitting off a molecule of ethylene.
- o Chain ending occurs through association or disproportionation of free radicals.

These initiation, chain propagation and termination reactions are considered to be occurring in complex gas-phase reactions. In the hydroxyrolysis reactions the free radicals formed in the initiation step and hydrogen may react together to follow the chain propagation process. Shabtai, et al. (56) have postulated that the reaction $R \cdot + H_2 \rightleftharpoons RH + H \cdot$ is a significant reaction of the hydroxyrolysis of n-decane.

Analysis of pyrolysis products of asphaltenes by Ritchie, et al., (57) strongly suggested that asphaltene contained in part long alkyl chains which are attached to aromatic rings (23,57). To rationalize the fragmentation pattern of asphaltenes, Ritchie suggested that homolytic

pyrolytic scission of the hydrocarbon substrates in asphaltenes gives an alkyl radical, which terminates either by hydrogen abstraction to yield the n-alkane or by hydrogen loss to yield the alk-1-ene as follows:



D. S. Ross and J. E. Blessing (58) have noted that the benzylic bonds have the lowest bond dissociation energies (60-70 kcal/mole) and are susceptible to homolytic fission due to the stability of these benzyl radicals. Fission of the aromatic ring itself requires much higher bond dissociation energies and in the absence of catalysts, no reaction is observed.

When deuterium gas was used as a tracer in the hydropyrolysis of coal in the absence of any catalysts, investigation of the liquefaction products by J. J. Ratto (59) showed incorporation of deuterium predominantly in benzylic structural positions. When similar pyrolysis was carried out in the presence of deuterated tetralin, preferential incorporation of deuterium was observed in the -alkyl (aliphatic) position of soluble coal products and nearly two-thirds of the protium incorporated into the -alkyl

position of tetralin-d .
12

In their studies of isomerization and adduction of hydroaromatic systems under coal liquefaction conditions, D. C. Cronauer, et al., (60) observed that the isomerization is dependent upon the breaking of benzylic carbon bonds and is promoted by the presence of free radicals. The rate of isomerization is first order with respect to the concentration of hydroaromatic rings. Most coal liquefaction products contain two to three aromatic rings with various degrees of saturation and therefore these hydroaromatics possibly play important roles as hydrogen donor in the free radical reactions believed to be operative during the pyrolysis of coals.

J. M. L. Penninger (61) and his co-workers studied the pyrolysis of indan in pressurized deuterium gas. The results indicated that the reaction proceeds by alpha and beta-ring opening mechanisms in which indan itself acts as a hydrogen donor by splitting off the hydrogen atoms required in the initiation of the ring opening, followed primarily by quenching radical intermediates by intermolecular hydrogen transfer. Radical quenching with deuterium gas was found to account for 25% of the primary products formed.

The foregoing observations led to the general notion that coal liquefaction proceeds by free-radical initiation by

breaking weak bonds within the coal/coal-tar substrates, followed by hydrogen abstraction from the carrier hydrogen gas donor molecule within the reaction matrix. The effectiveness of tetralin compared to naphthalene or decalin as a hydrogen donor has been rationalized on the basis of its possessing benzylic hydrogen atoms, whereas indane having just as many benzylic hydrogens as tetralin has proven to be a poor hydrogen donor (62). To account for this apparent dichotomy, researchers have focussed their attention to other possible reaction pathways. On the basis of Woodward-Hoffman's orbital symmetry rules for concerted pericyclic reactions, P. S. Virk and his co-workers (63) explained that anthracene undergoes pericyclic transfer reaction with dihydronaphthalene following the orbital symmetry rules of Woodward and Hoffman. This is illustrated as follows: (63)

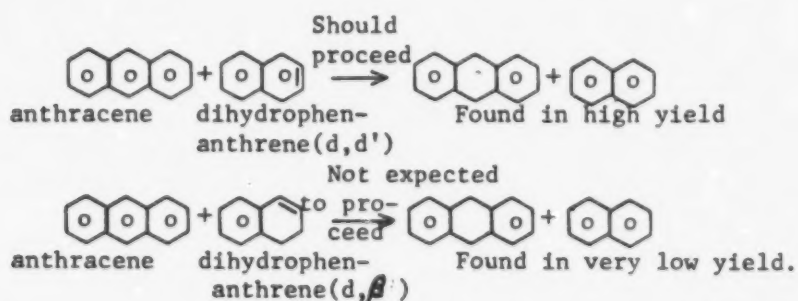


Figure 16: Pericyclic Reactions

The model studies discussed above provide some valuable insights into the reaction mechanism applicable to the pyrolysis of coal, coal-tar, tar sands and petroleum residues. It can be realized though that the break down of condensed polynuclear aromatic hydrocarbons, comprising a significant content of maltenes and asphaltenes, is neither very easily achieved nor is amenable to simple mechanistic interpretation.

Penninger and Slotbom (64) investigated the high pressure thermal hydrogenolysis of phenanthrene. They concluded that both tricyclics are cracked mainly by stepwise hydrogenation of outer rings, ring opening and side chain cracking. Cracking within the side chain was extensive in contrast to the dealkylation of side chains, normally observed over acidic catalysts (65,66) which are believed to occur via carbonium ions rather than free radicals as reaction intermediates. As depicted in Figure 17, the pathway involving the intermediate 1 dominates the reaction sequence since no 1-substituted naphthalenes were detected.

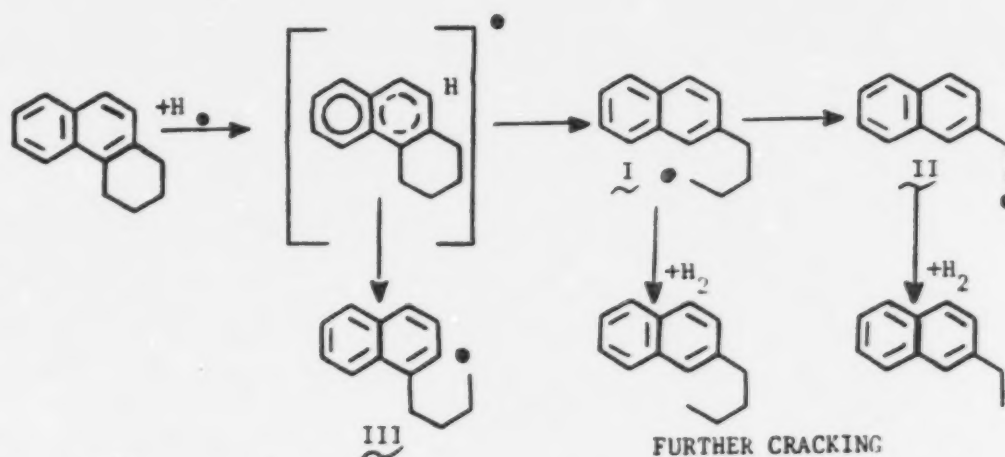


Figure 17: Thermal Hydrogenolysis of Tetrahydro Phenanthrene., Penninger and Slotboom (64).

In addition to terminal ring cleavage, substantial quantities of ethylbiphenyl, biphenyl and diphenylethane were formed suggesting cracking of the central ring according to the scheme in Figure 18.

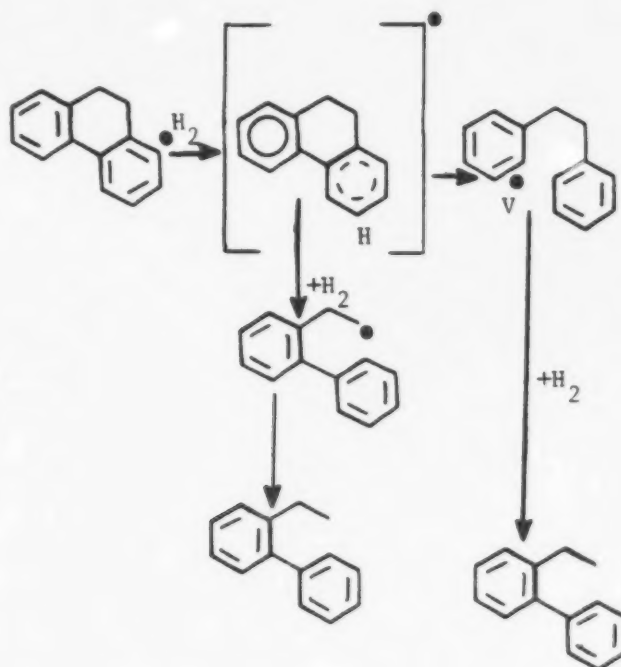


Figure 18: Thermal Hydrogenolysis of Dihydrophenanthrene, Penninger and Slotboom (64).

Showronski and Recht (67) hydrocracked phenanthrene in the presence of a 50:50 mixture of $\text{MOH}:\text{M CO}$ (where $\text{M}=\text{Li}, \text{Na}, \text{K}$) in a batch autoclave at 475 C and 20.7 MPa (3000 psi). The product distribution was similar to those of Penninger and Slotboom as shown in Figure 19. The cracked products were mostly alkyl naphthalenes, 2-ethyl biphenyl and smaller quantities of diphenyl ethane.

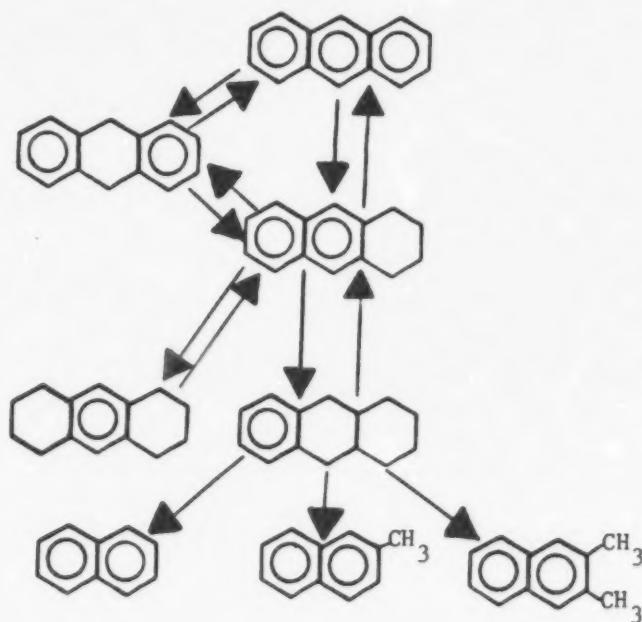


Figure 19: Hydrogenolysis of Condensed Ring Aromatics Over Supported Nickel (64).

R. N. Pandey of Guelph Chemical Laboratories carried out flash hydropyrolysis of naphthalene, phenanthrene, chrysene and perylene over sulfided Ni-W and Co-Mo catalysts (31). The flash hydropyrolysis experiments were conducted at a heating rate of 1000 °C in one to two seconds, followed by rapid quenching of products. The reaction remained virtually under the kinetic control allowing heterogeneous catalysis to occur over the catalyst surface and in gaseous hydrogen diluent from the condensed to vapour phases.

Dihydro-, tetrahydro-, octahydro- and perhydro-phenanthrene were observed as the hydrogenation products, supporting the stepwise successive hydrogenations steps on the terminal and inner rings. The absence of large branched paraffins indicated that ring opening of perhydrophenanthrene did not take place under the applied experimental conditions. The presence of substantial quantities of naphthalene, 1- and 2-substituted naphthalenes, tetralin and substituted tetralins as also toluene and xylenes served as evidence that the major reaction path followed the partial hydrogenation of end rings, ring opening and side chain cracking, as were also observed by Penninger and Slotboom (64). The large amounts of gases (methane, ethane, propane, butane) which were produced substantiated the assumption of a predominance of the terminal ring opening and dealkylation mechanisms. Lighter than butane gases were formed, probably by a side chain cracking of n-butyl-naphthalene and n-butyl-tetralin or by secondary reactions of n-butane. In addition, minor amounts of ethylbiphenyl and biphenyl were formed indicating the central ring opening. The presence of some substituted naphthalenes and tetralins in other than the 1 or 2 position indicated also that secondary alkylation reactions were taking place. R. N. Pandey proposed a general pathway for the formation of products in FHP of phenanthrene as shown in Figure 6.

Sekhar and Ternan (68) pyrolysed pitch derived from hydrocracked Athabasca bitumen in an inert atmosphere at temperatures ranging from 350 - 1000 °C. Studies of the heat and mass transfer effects on the reaction rate indicated that bulk of the pyrolytic reactions occurred below 500 °C producing liquid and gaseous products. Above 500 °C, the rate of decomposition was found to be slower and gradually decreased with time. Based on the Arrhenius plot of kinetic data, the authors concluded that the overall pyrolysis proceeds in two distinct stages. During the first stage, the apparent activation energy increased with the extent of reaction, approaching a maximum when about 20% of the sample decomposed. Under these conditions, the pyrolysis was found to follow first-order kinetics with respect to the unreacted pitch. The activation energy and the pre-exponential factor, which were found to be functions of the extent of decomposition, exhibited a well defined compensation effect attributable to the surface properties in the condensed and vapour phases. During the second stage, the activation energy decreased with increasing extent of the reaction and the kinetics were too complex to permit any simple explanation.

Bunger and his co-workers (69) studied the effect of asphaltenes on conversion of bitumen by hydropyrolysis. They found that the addition of asphaltenes had a marked effect on

increasing the gas formation, relative to liquids and therefore, required appreciable quantities of hydrogen for conversion. Very little hydrogenation of aromatics, abundant in asphaltenes, occurred and it was concluded that hydropyrolysis inhibits the generation of large quantities of aromatics.

In discussing the inhibition of coke formation in hydropyrolysis processing of heavy oils, Bungler (70) maintains that when liquid feedstock is preheated to 420 °C and subsequently dispersed in a flowing stream of hydrogen preheated above 600 °C, the droplet oil is not exposed to temperatures higher than 420 °C without contact with hydrogen. Bungler postulates that the coke forming reactions are inhibited as a result of the following sequences of physico-chemical processes:

- o Dilution of aromatics through vapourization in hydrogen.
- o Aromatic free radicals are terminated through metathesis* reactions with molecular hydrogen, thus they are not available for reactions with other aromatics.
- o The concentration of vinyl arenes is reduced through attack on vinylic bond by hydrogen, thus rendering the species unreactive to diene-type reactions.

* S. W. Benson defines (55) metathesis as replacement of the less reactive alkyl radicals by the more reactive H atoms when reactions of the type $R + H_2 \rightleftharpoons RH + H$ occur under pyrolytic conditions. He further states that such reactions may effect 100 to 200 percent rate enhancements.

- o Hydrogen atom preferentially hydrogenates polycondensed aromatics and thereby inhibits the formation of aromatics.

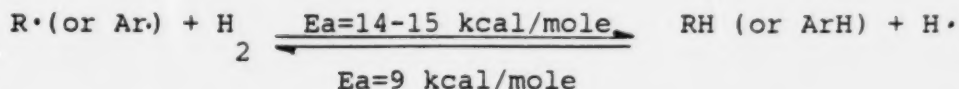
The factors as above appear to be consistent with the observation that in hydropyrolysis, coke formation occurs at the walls of the reactor where longer residence times in the liquid phase result in incomplete dispersion of aromatics and poor contact with hydrogen.

Bunger (71) has summarized the effects in hydropyrolysis as follows:

- o Reduction of coke formation
- o Reduction of dehydrogenation of naphthenes
- o Hydrogenation of aromatics and olefins
- o Promotion of dealkylation

As the kinetics and mechanism of these reactions are fully understood a process can be effectively developed for yielding desirable products - consistent with the objective of studying reaction kinetics of complex systems in general and flash hydropyrolysis in particular.

Based upon the kinetic data, Bunger (70) has attributed the reactions with molecular hydrogen to be the principal reaction step:



Where E_a is the activation energies of the alkyl radicals. It is through this pathways that the free radicals are believed to become saturated and hydrogen atoms are produced in the FHP process - rather at modest temperatures and in the vapour phase. It is then readily seen that good contact of hydrogen with free radicals is required to accelerate the forward metathesis reactions and is believed to occur in significant amounts above 435 °C.

In addition to hydrocracking of polynuclear aromatics, hydrodesulfurization (HDS), hydroenitrogenation (HDN) and hydrodeoxygenation (HDO) of heterocyclic as well as non-heterocyclic S-, N- and O- containing compounds play an important role in the conversion of high molecular weight material to lighter products. Removal of these heteroatoms from feed require the use of suitable catalysts during hydropyrolysis of coal, coal-tar and petroleum residues. D. G. Gavin (83) in his review of coal hydrogenation catalysis has summarized and the reader is directed to this extensive review for the details of the various mechanistic pathways believed to predominate in pyrolytic and hydropyrolytic reactions employing catalysts. These are briefly discussed as follows:

HDN is believed to proceed by hydrogenation of the N-containing ring followed by C-N bond scission (83). For example, indole is hydrogenated via indoline, o-ethylaniline to ethylcyclohexane. $\text{SiO}_2 - \text{Al}_2\text{O}_3$ and Al_2O_3 containing Group VIII transition metals are effective HDN catalysts with Mo on gamma Al_2O_3 proven to be the most effective one. HDO appears to be studied with the intent of reducing H_2 consumption as the production of H_2O in the hydrogenation reaction is not an environmental problem. Phenols, carboxylic acids and fused-ring furans constitute the predominant sources of oxygen-containing organic compounds present in maltenes and asphaltenes. Deoxygenation has been found to be the most difficult of the heteroatom reactions studied and it has been noted that partial hydrogenation of benzofuran is obligatory pre-requisite to HDO (83).

In contrast to HDN and HDO, hydrogenation of the ring containing the sulphur heteroatom is not a pre-requisite to hydrogenolysis in HDS reactions. HDS of benzothiophene, dibenzothiophene and benzonaphthothiophene was effectively catalyzed by Co-Mo- Al_2O_3 catalyst at 400 C. The main products of HDS reactions consisted of various hydrogenated aromatics and H_2S (83).

The heteroatom contents of coals and biomass can be as high as 15% and 40% respectively (73). Efficient removal of

these heteroatoms in FHP process will not only result in clean burning fuel, but would also enhance the yield of BTX and gaseous hydrocarbons since the end-products of HDN, HDO and HDS reactions are hydroaromatics, which can undergo hydrocracking reactions analogous to those of hydrogenated polynuclear aromatics, discussed in previous section.

II.5 Catalytic FHP

The use of catalysts has been well documented in the liquefaction of coal and petroleum residues. The need for conversion of heavy oil, coal and residuum has resulted in the search and development of new technology such as FHP which involves addition of hydrogen in contrast to rejection of carbon in the conventional techniques. However the feed available for conversion contain significant amounts of asphaltene and metals. The use of catalysts for FHP requires solution of usual problems encountered in upgrading of heavy residuum. This has stimulated the development of various types of catalysts to remove asphaltenes and metals, and also to resist poisoning due to carbon and metal deposits (73).

In coal liquifaction, an important consideration is to remove sulphur and nitrogen from the cracked oil so that clean and pollution-free light fractions are obtained (74,75). The presence of trace amounts of Na, Ni and V in crude oil has significant effect on catalyst performance

because of the accumulation of these metals in the feed streams and on the catalyst surfaces (77), thus necessitating the development of various catalyst regeneration processes.

Asphaltenes are believed to be organo-metallic macromolecules, their effective diffusion co-efficient in the pores of catalyst is of the order of $10^{-7} \text{ cm}^2/\text{sec}$ (77). Therefore, the asphaltene conversion may be diffusion controlled. The development of effective commercial catalysts with a specific pore structure are required to maintain activity for asphaltene conversion, desulphurization and demetallation (removal of vanadium and nickel) over a period during which carbon and metals may continue to deposit. While the testing of a number of catalysts has been reported, many others are proprietary in nature and are not available for research purposes. Some of the catalysts used are SnCl_2 , ZnCl_2 , KOH , $(\text{NH}_4)_2\text{MoO}_4$, $\text{Fe}(\text{OH})_3$ -S, MoO_3 , metallic Zn, sulfided N-W and Co-Mo and alumina. Although the role of hydrogen donor solvents in the reaction matrix has generally been viewed as catalysis of the cracking reactions to produce liquid hydrocarbons, such donors are known to participate in free radical transfer reactions resulting in their degradation. These reactions were discussed in the earlier section under kinetics and reaction mechanisms.

Shinn and Vermeulen reported (78) that melt treated coal in ZnCl_2 - methanol was pyrolyzed at 400-500 °C and 5.5 MPa (800 psig) with high liquid yields favouring aromatic-hydroaromatic equilibria towards the formation of aromatics. At temperatures above 500 °C, the catalysis was found to be non-selective.

Morita et al. (79) studied the kinetics of direct liquefaction of coal in the presence of Mo-Fe catalysts. The results indicated that under temperature ranges of 350 ° to 410 °C, the reaction rate increased with increasing temperature and oil yields enhance with an increase in nominal reaction time with $\text{Fe}(\text{OH})_3$ - MoO_3 - S (1:1:1) being the most active catalyst (compared to MoO_3 , $\text{Fe}(\text{OH})_3$ - S, $\text{H}_2\text{MoO}_4 \cdot \text{H}_2\text{O}$ and $\text{Fe}(\text{OH})_3$ - $\text{H}_2\text{MoO}_4 \cdot \text{H}_2\text{O}$). The simulation of liquefaction calculated by substituting the assumed rate constants into the rate equation fitting a series of consecutive reaction scheme showed good agreement with experimental data. These are shown in figure 20.

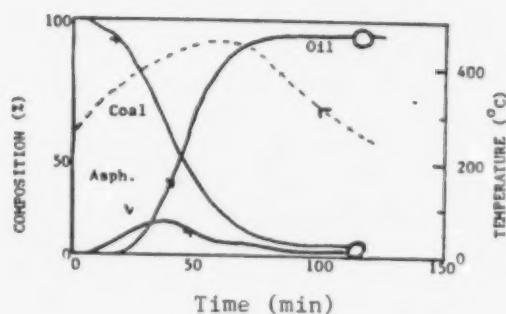


Figure 20: Comparison of experimental liquefaction course for Miike coal with simulated one: (0, 0, 0, ---), experimental data; (-), simulated course.
 Reaction Time = 16 min;
 Reaction Temperature = 450°C
 catalyst = MoO₃ (79).

Kershaw, et al. (11) reported the effect of SnCl₄ on the hydropyrolysis of coal in the temperature range 400² - 700⁰ C and 25 MPa hydrogen pressure using a fixed bed reactor. Increasing the catalyst concentration substantially enhanced the quality and yield of oil with reduced heteroatom content, while the gross hydrocarbon structure was little affected. High temperature and long residence time had dramatic effect on the quality of oil in terms of increased lighter products with high aromatic content.

M. Nomura and co-workers (80) conducted a detailed study of the effect of a ZnCl₂-KCl-NaCl ternary melt (3:1:1 mol. ratio) on the hydrocracking of Athabasca asphaltene at 400⁰ C

and 9.8 MPa hydrogen pressure for one hour. The results indicated that up to 50% of asphaltenes were converted to lighter fractions with decreased sulphur in the product liquid fractions. A marked increase in mono and di aromatics was caused by the molten salts at the expense of polyaromatics and polar materials present in the asphaltene feedstocks. Added MoCl_5 increased the amount of saturates in the liquid fractions and is believed to inhibit coke formation. Considerable decomposition of tetrahydrothiophene also occurred when CaCl_2 was added to the melt.

It is generally recognized that alumina promotes condensation of larger molecules on the catalyst surface and Co-Mo promotes hydrogenolysis of polyaromatics. With this view, Khulbe and his co-workers (81) carried out hydrocracking of Athabasca bitumen using a Cobalt-Molybdenum-Alumina catalyst mixture in the feedstock. The results were inconclusive due to extensive reactor plugging. It is contemplated that natural zeolites may provide the surface porosity comparable to alumina and their use in conjunction with suitable metals may serve as cost-effective catalyst materials necessary for the hydrolysis of heavy residues (76). The need for the development of low-cost disposable catalysts with effective de-sulphurization capability has also been pointed out (74).

D. G. Gavin has presented an excellent review (83) of a variety of catalysts used in the liquefaction of coals. Although the use of catalysts in flash hydropyrolysis of coal, coal-tar and petroleum residues is a recent approach, considerable insight may be gained from the catalytic properties of various materials used in the hydrogenation of coal. Of particular interest is the use of cheap disposable catalysts such as Ni-bearing ores, metal-doped clays and iron sulphide in "Red-Mud" from bauxite refining (41-60% Fe_2O_3) are notable. D. G. Gavin (83) noted that Molybdenum^{3 4} and Tungsten based catalyst have been widely used and appeared most effective in asphaltene conversion as well as hydrodesulfurization. In addition, small pores size of catalyst surfaces may cause exclusion of large asphaltene micelles (M.W. 1100) resulting in hindered diffusion and reduced catalytic efficiency. It has been noted though that Ni-Mo-Al₂O₃ catalysts having pore sizes in excess of 0.2 microns have been found to be most effective (normal pore diameters of catalyst vary between .003 to 0.02 microns and possibly exclude asphaltene micelles).

Flash hydropyrolysis requires the use of catalysts when asphaltene is a significant constituent of the feed materials. In addition to removing S, O and N heteroatoms, catalysts can promote hydrogenolysis of polynuclear aromatic and their subsequent cracking to yield monoaromatics and

alkanes. The results of various flash hydrolysis studies are summarized in Table 1 , indicating the effectiveness of various catalysts in enhancing conversion of coal. These studies show that FHP in the presence of catalysts offer significant advantages over non-catalytic reactions. This report describes the FHP of Cold Lake Pitch in the presence of various catalysts and experimental conditions.

TABLE I: A Summary of Results of Flash Hydrolysis Studies of Coal/Coal-tar/bitumen/petroleum residue.

Reactor Type	Feed	Catalyst	Optimum Conditions for max. BTX yield					Yield(%)		Remarks	Reference Number
			Temperature °C	H ₂ Pressure MPa	Heating Rate °C/sec.	Vapour Residence Time(sec.)	BTX	Heavy Oil	Gases		
Electric Current Heater (2 Stage)	British Coals	Activated Carbon (900%)	Stage I: 600 Stage II: 850	15	5	7 (Stage II)	12 (benzene)	N.R.*	~36	Benzene yield increased with 2-stage reactor, up to 4.5% BTX ^a yielded at 600°C, 7°C/sec and 11 sec. vapour residence time	10
			400-700	25	3-4	N.R.*	N.R.*	N.R.*	N.R.*		11
Electric Current Heater (Hot Rod)	New Wakefield Coal	SnCl ₂ (15%) and Sand	400-700	25	3-4	N.R.*	N.R.*	N.R.*	N.R.*	H ₂ flow: 22 L/min. Light aromatic yield increased with increased temperature and reaction time.	11
			580	3.45	1,000	30 (reaction time)	N.R.*	N.R.*	N.R.*		12
Entrained Gas Downflow	Solid peat	-	870-925	3.4	N.R.*	1-4	12-15	N.R.*	40-50	Total composite yield reached a max. of 29% (liquid and gases) up to 85% carbon conversion achieved	14
			760	7.9	N.R.*	2-3	28	28	24		15
Vertical Entrained Gas	Western Kentucky Coal	ZnCl ₂ (10%)	760	7.9	N.R.*	2-3	28	28	24	Solid residence time = 20 sec.	15

TABLE I: A Summary of Results of Flash Hydrolysis Studies
of Coal/Coal-tar/bitumen/petroleum residue. (cont'd)

Reactor Type	Feed	Catalyst	Optimum Conditions for max. BTX yield				Yield(%)		Remarks	Reference Number
			Temperature °C	H ₂ Pressure MPa	Heating Rate °C/sec.	Vapour Residence Time(sec.)	BTX	Heavy Oil		
Downflow Entrained Tubular	New Mexico Sub-bituminous Coal	-	1,000	1.4	~10 ⁴	2-3	7-8	5	H ₂ gas provided faster heating rate and max. liquid yields compared to Ar or CH ₄	16
Downflow Entrained Gas	North Dakota Lignite	-	700	10.4	~200	3-6	3.4	11.5	Lignites rich in oxygenated compounds are converted to BTX in H ₂ as a function of temperature and pressure. Results are independent of heating rate above 70°C/sec.	17
Electric Current Heater (fixed bed)	Canadian Coal	-	800	10	600	N.R.*	12	N.R.*	Primary purpose was to study influence of heating rate on coal. No vapour residence time reported.	12
Batch Downflow Reactor	Virgin Bitumen (Utah Tar Sand)	a) Silica-Alumina	425	1	N.R.*	N.R.*	N.R.*	N.R.*	Composite liquid yield is 79%; Runtime = 11 min.	25
		b) Molecular Sieve	425	1	N.R.*	N.R.*	N.R.*	N.R.*	Composite liquid yield is 80%; Runtime = 11 min.	25
		c) -	525	12.4	N.R.*	5	N.R.*	N.R.*	Composite liquid yield is 85.6%	45

TABLE 1: A Summary of Results of Flash Hydrolysis Studies
of Coal/Coal-ter/bitumen/petroleum residue. (cont'd)

Reactor Type	Feed	Catalyst	Optimum Conditions for max. BTX yield				Yield(%)			Remarks	Reference Number
			Temperature °C	H ₂ Pressure MPa	Heating Rate °C/sec.	Vapour Residence Time(sec.)	BTX	Heavy Oil	Gases		
Bottom Feed Vertical Reactor	Athabasca Bitumen	Co(NO ₃) ₂ ·(NH ₄) ₆ Mo ₇ O ₂₄ ·Al ₂ O ₃ (15%)	460	13.79	N.R.*	N.R.*	N.R.*	N.R.*	N.R.*	Naptha : 18.2% Oil and Resin : 76.5% 72% Sulfur Removal achieved	48, 49
Two-Stage-Quartz Reactor Tube	Residual Heavy Oil	Silica - Alumina Bed in 2nd Stage	800	Argon Flow	N.R.*	0.35-1.0	N.R.*	N.R.*	60	Olefin yield predominated	30, 51
Downflow Entrained Tubular	North Dakota Lignite and New Mexico Sub-bituminous coal	-	765-775	10.3	4X10 ⁴	7-8	10-12	10-12	34-36	Optimum pressure was reached at 10.3 MPa or 1,500 psig.	28, 29
Electric Current Heater	Naphthalene Phenanthrene Chrysene	Ni-W-S/Alumina or Co-Mo-S/Alumina (10%)	752-791 588-750 780-850	6.89 6.89 6.89	800 800 800	2 2 2	21 2 -	5 23 ~17	27 37 33	Ni-W-S and Co-Mo-S were equally effective Heavy oil yield includes alkyl polyaromatics, hydroaromatics and C ₄ + alkanes	31
Electric Current Heater	U.S. Coals	-	750-850	101.3	650	0.6	16-17	10-11	20	BTX yield is max. for intermediate rank sub-bituminous coals	53
Electric current Heater	Asphaltenes from Australian Coals	CoO, MoO ₃ /Al ₂ O ₃	400	13.8	1-2	20-30	N.R.*	N.R.*	N.R.*	Aromatics: 10-26% Aliphatics: 74-90% Alkanes: C ₉ - C ₃₂ possibly found to aromatic ring.	54

TABLE 1: A Summary of Results of Flash Hydrolysis Studies
of Coal/Coal-tar/bitumen/petroleum residue. (cont'd)

Reactor Type	Feed	Catalyst	Optimum Conditions for max. BTX yield					Yield(%)		Remarks	Reference Number
			Temperature °C	H ₂ Pressure MPa	Heating Rate °C/sec.	Vapour Residence Time(sec.)	BTX	Heavy Oil	Gases		
Fluidized Bed 2-Stage	Fine Coal Particles	Second Stage Cracking in Sand Bed	1st Stage: 600 2nd Stage: 1,000	Fluidizing N ₂	10 ⁴	1-2	6-7 (benzene)	N.R.*	24-30	Olefin yield predominated from tars containing up to 35% alkanes	32, 33
	Heavy Petroleum Oil	-	700-777	4.1-4.8	850	0.5	15	~3	67	Oil hold up time in reaction zone: 7-8 sec.. Increasing vapour residence time increased carbon residues	34

* N.R. = NOT REPORTED

III.0 EXPERIMENTAL WORK

III.1 Setting up Apparatus and operation of fast Temperature Measuring Device

Previous FHP work (31) on model compounds from this laboratory described the details of the bench scale FHP apparatus used with all its features: control of heating rate, reaction time, temperature measurement and technique of rapid quenching of products. In that study the temperature measurement device was subject to some ambiguities. In order to develop a system to measure a heating rate, transition from initial to isothermal temperature an improved version of earlier temperature measuring system was devised using oscilloscope. The principal features of the modified apparatus include:

- o a temperature vs. time profile which can be accurately measured from a type K thermocouple attached from the two points of the reactor to the Tektronix dual channel oscilloscope.
- o the temperature triggered response vs. time event is photographed on a camera from which temperature thus a heating rate is calculated.
- o a preheated (to 400 C) hydrogen gas at 1000 psig is used at the time of flashing.

III.1.1 Reactor System and Experimental Procedure

A schematic diagram of the flash hydrolysis apparatus used in the present investigation is shown in figure 21. The reactor is 375 mm long and 63 mm outer diameter stainless steel tubing. A 10 to 100 mg of pitch

sample mixed with known weight of catalyst was placed in an aluminum boat at a selected point in the tube and hydrogen at pressure was allowed to flow continuously, as shown in figure 21, towards the analytical system. Provision was made at the entrance of the reactor for a pressure relief valve which was set to open at a preset pressure. The reactor tube was heated rapidly by passing a large current through it and the temperature was monitored by means of Techtronic dual channel oscilloscope. The heating current was controlled by solenoids activated by two timers. The main heating system provided heating rates 100-600 °C per second controlled by first timer. After reaching the preset temperature the secondary heating current which used lower voltage power supply maintained the isothermal reaction temperature for the period of experimental run and was controlled by second timer. The condensable products were quenched in a trap and kept at a low temperature whereas non-condensable gases were collected in evacuated cylinders. The distance of the electrical lead from the sample and the hydrogen flow rates were varied to obtain a desired vapour residence time.

NOTATIONS FOR FIGURE 21

PG	Pressure Gauge
MV	Metering Valve
CV	Check Valve
SF	Swagelok Fitting
F	Filter
BPR	Back Pressure Regulator
3WV	3-way Valve
BV	Ball Valve
CC	Collection Cylinders
CT	Reaction Tube for char combustion
C	Clamp
E	Electrical Connection
K	Type K Thermocouple
DT	Digital Thermometer
T	Timer
SHPS	Secondary Heating Power Supply
MHPS	Main Heating Power Supply
GC	Gas Chromatograph
OSC	Oscilloscope
C	Charcoal Tube

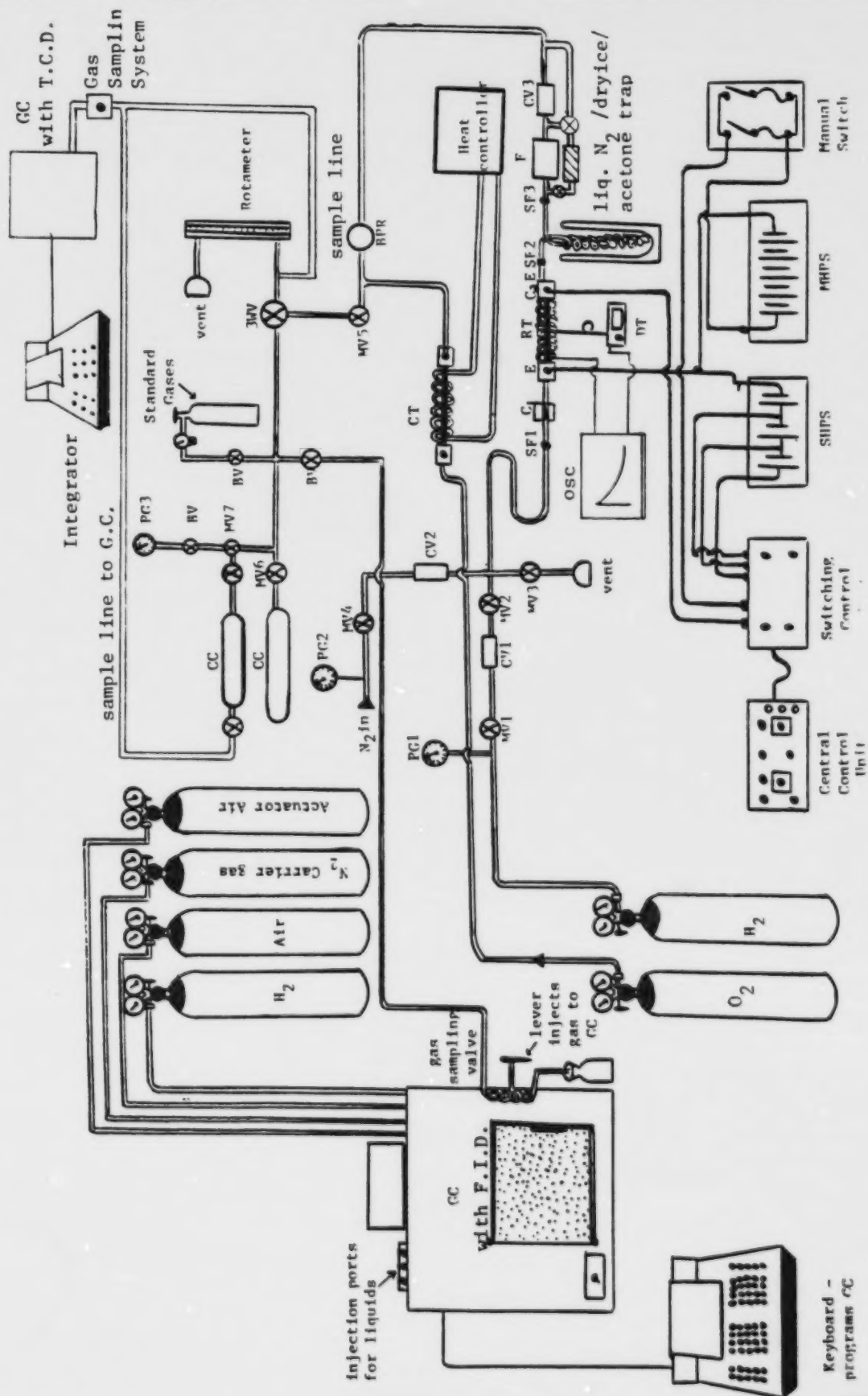


Figure 21: FHP Apparatus -- with all its components.

Figure 21a

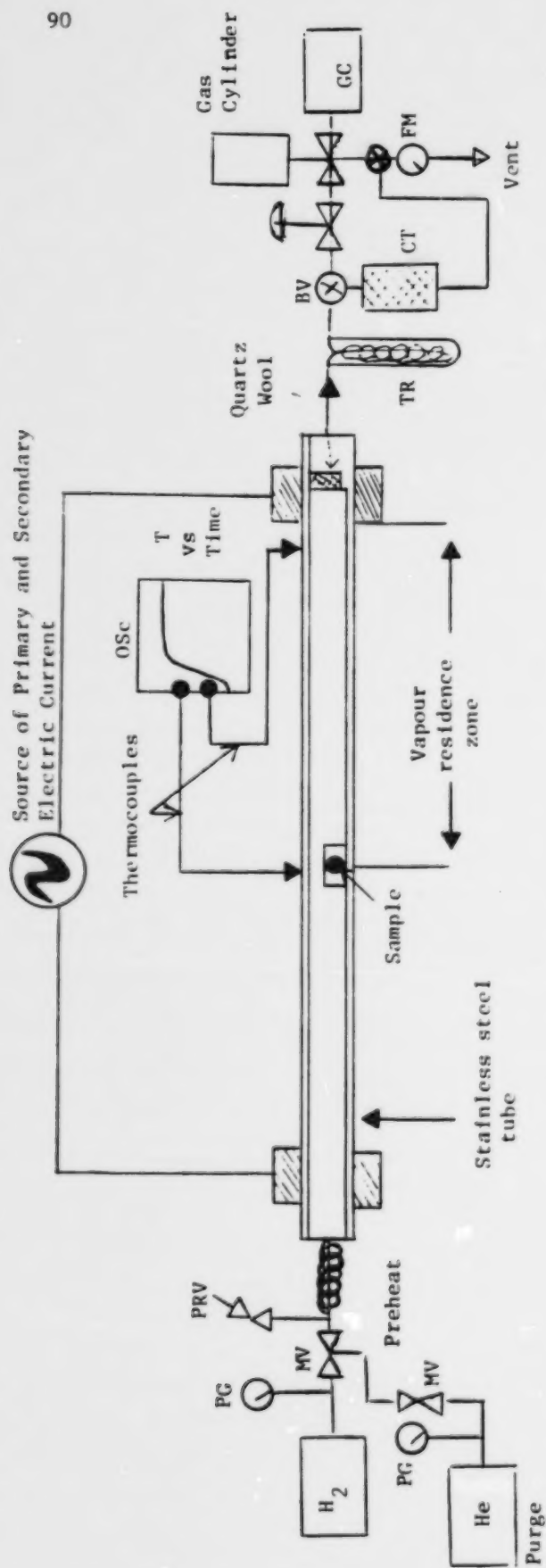
Schematic Diagram of FHP Apparatus

Legend:

OSC = Oscilloscope
BPR = Back Pressure Regulator
FM = Flow Meter
CT = Charcoal Trap
TR = Condenser Trap
BV = Bi-directional Valve
PRV = Pressure Relief Valve
MV = Metering Valve
PG = Pressure Gage

FIGURE 21a

Schematic Diagram of Reactor Heating, Residence Zone and Temperature Measurement.



III.1.2 Calibration of Thermocouples

The thermocouples were calibrated using a linearized digital thermometer and channel 1 and 2 on the oscilloscope. Melting points of metals ($Zn=420^{\circ}C$, $Al=660^{\circ}C$, and $Cu=1083^{\circ}C$) were used for the calibration over the entire temperature range. The boiling point of water was checked as a measure of linearity in the lower range of temperature. The reference material was placed inside an insulated graphite crucible with heating device. The metal was brought to a temperature of $15^{\circ}C$ above the melting point for several minutes and then cooled slowly. Thermal e.m.f. were measured on channel 1 and 2 of oscilloscope corresponding to the melting and freezing point as observed in the levelling off the temperature vs. time plot. If the two temperatures did not agree then another determination was made. The digital thermometer was found to be linear over the temperature range. The results are given in Table 2.

Table 2

Thermal e.m.f.'s at various Temperatures

Actual Temperature ° (C)	Digital Reading ° (C)	Oscilloscope	
		Ch.1 (mv)	Ch.2 (mv)
98	100	3.25	3.25
420	420	16.50	16.50
660	666	26.75	26.75
1083	1076	44.00	43.00

mv are measured from oscilloscope screen

The plots indicating linearity are shown in figure 22.

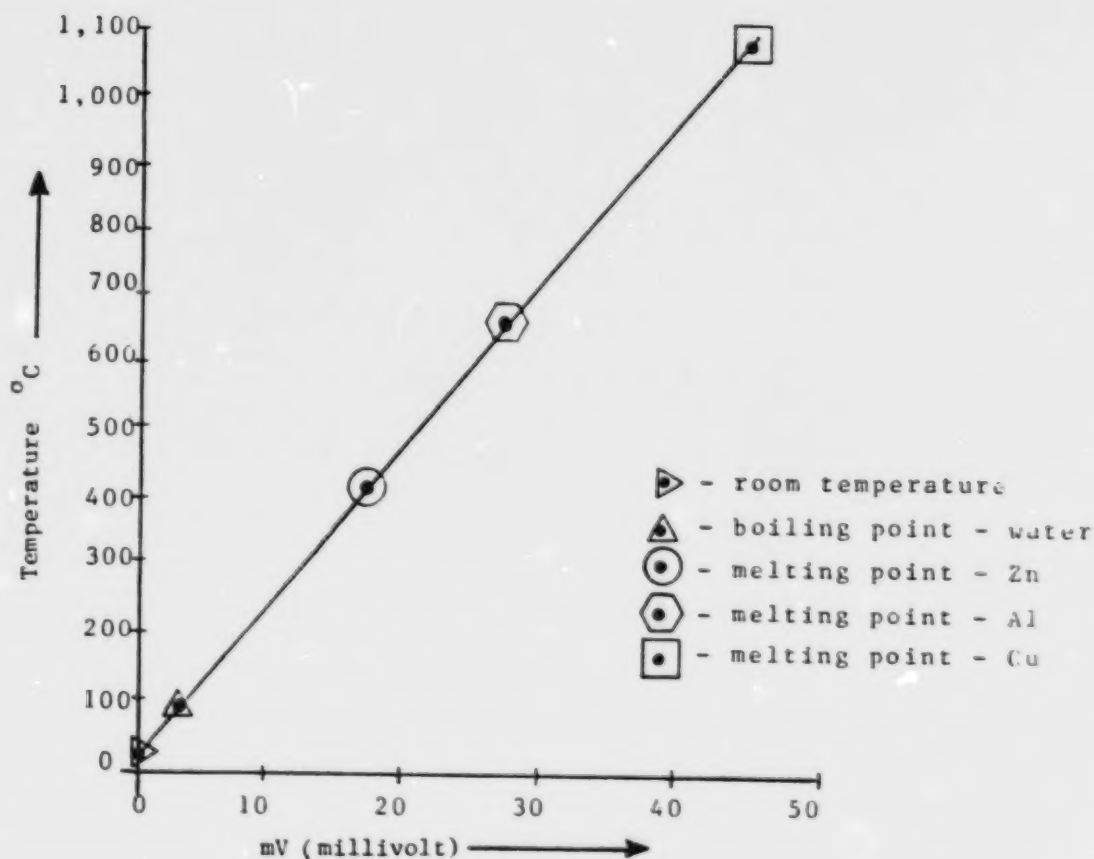


Figure 22: Plots of temperature vs. millivolts on oscilloscope.

III.1.3 Temperature and Heating Rate Measurements

In order to measure a heating rate, transition from initial temperature to final temperatures, Tektronix dual channel oscilloscope model 2213A was used. Type K thermocouples used to feed the voltage response were calibrated as above. Thermocouple leads from two locations

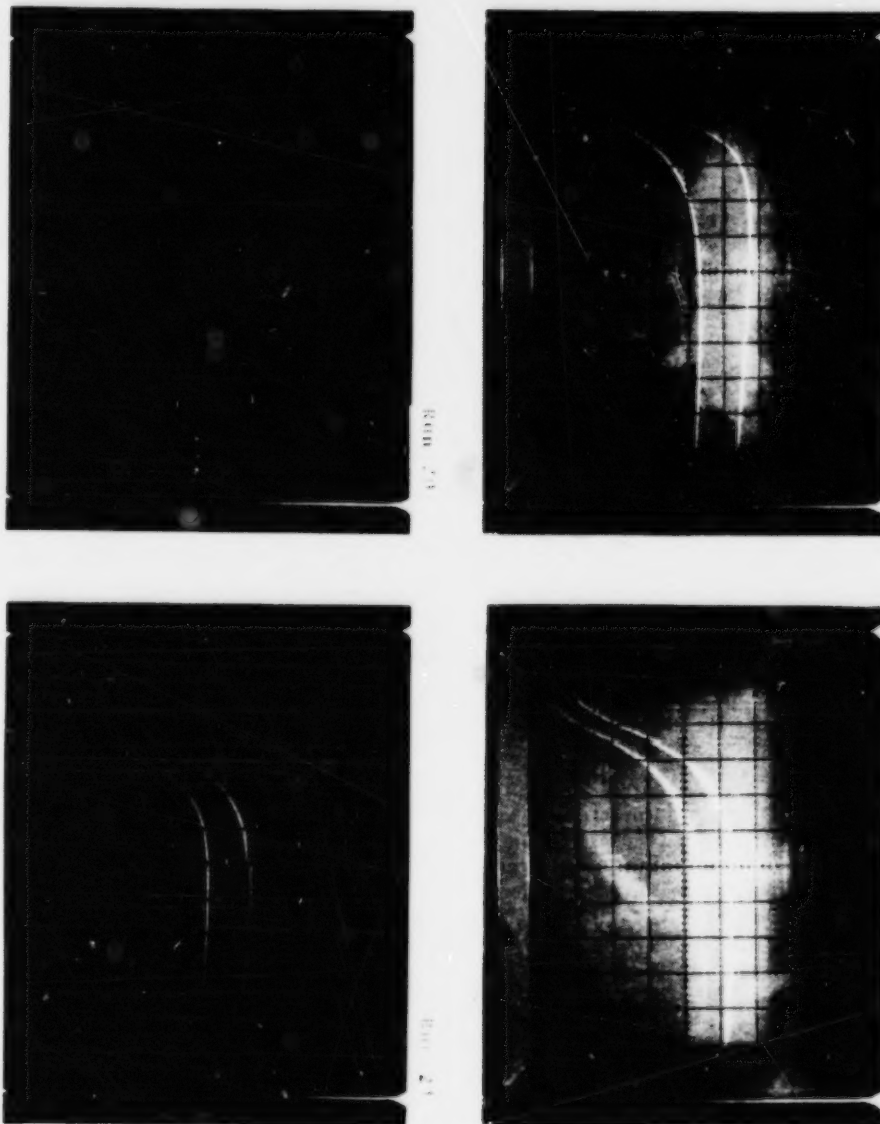
of the reactor were connected to channel 1 and 2 on the oscilloscope and the temperature triggered milivolt response vs. time event was photographed on Tektronix C-5C oscilloscope from which the temperature profile and thus the heating rate was calculated. A typical heating event as displayed on an oscilloscope is shown in figure 23. A typical temperature vs. time profile as deduced from oscilloscope trace is shown in figure 24.

III.1.4 Pitch Temperature

An investigation was made for possible heat limitation to the pitch sample. In an experiment one of the thermocouple was placed inside reactor tube dipping in the pitch sample and the other to the outside reactor at the sample location. The pitch was heated rapidly by conducting a typical run. The temperature recorded by the two thermocouples were found to be within $\pm 10^{\circ}\text{C}$.

Figure 23

A Typical Heating Event
as Displayed on Oscilloscope
o trace scale = 5mv/div.
o time scale = 1 sec./div.



channel 1: uppertrace connected at sample location
channel 2: lower trace connected at varying distance
from the sample

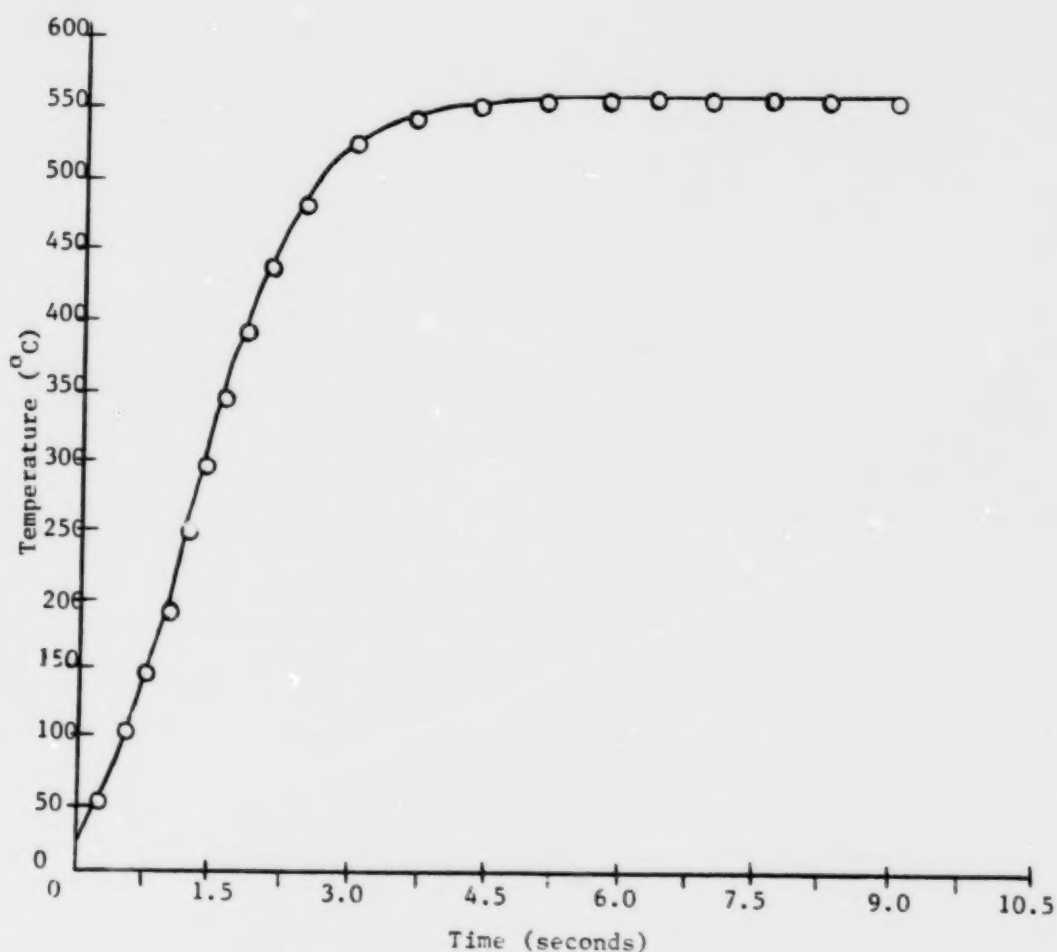


Figure 24: A typical Temperature (°C) vs. Time (seconds) profile from oscilloscope.

III.1.5 Effect of Sample Size on Initial and Isothermal Temperature of Reactor

A series of experiments were conducted (without product analysis) to check if sample size had any lag effect on

initial heating rate and final near isothermal temperatures. The sample weight was varied to 10 fold (to 200 mg). Temperature lag effects were not observed for total (sample and catalyst) weight up to 200 mg.

Planned experiments were performed with samples of total weight lower than this.

Oscilloscope traces indicated the following:

- o an isothermal reaction temperature (>10 sec.) is attained after initial heating period (<2 sec.) which is variable and can be lowered to 0.5 sec. if required, by applying higher current.
- o the vapour residence time is shorter than the isothermal period.
- o 80% of the temperature is attained within 1.5 sec. in majority of runs and this period is dependent on heating rate.

III.1.6 Difficulties Surmounted

Some difficulties were encountered in the application of oscillographic measurement. Of particular interest here to mention are the following:

- o thermocouples welded to reactor were found to produce noise and electromagnetic pick-up.
- o a significant leakage was found to occur through thermocouple contacts.

These difficulties were solved by electrically insulated cement contacts in place of spot welding.

III.1.7 Safety Features*

In our FHP system the primary and secondary heating is controlled by solenoid system. Changing to alternative, system, is being considered at future date. At present time, to prevent accidental welding of solenoid leading to uncontrollable heat resulting in reactor blowout, the following safety measures have been introduced in the system prior to experimental runs on pitches:

- o fuse blow system has been installed which blows out power at temperature $>1,000^{\circ}\text{C}$. A number of fuses were tried: 10, 60, 100, 150, and two 100 amperes. The 175 amp fuse was found suitable and is currently used.
- o double plexiglass shields are now used with up and down movement to allow flexibility and better reach to the system.

* It can be mentioned that in efforts to implement safety, laboratories engaged in FHP work in the United States have almost isolated their units and the operation via a remote control unit.

III.1.8 Installation of T.C. Detector

A thermal conductivity detector was installed in the line following the quenching trap and pressure reducer. This detector is used for monitoring the arrival of the product gases for switching to collecting cylinders. This detector is also used for analysis of char.

III.2.0 ANALYTICAL PROCEDURE

III.2.1 Analysis of Pitch Sample

The pitch used in the present investigation was obtained from the liquid products boiling above 525 °C from Cold Lake, Alberta. Prior to FHP runs the Cold Lake pitch was analyzed for gross parameters. The results are given in Table 3.

Table 3

Properties of the Cold Lake Pitch Sample
Used in this Investigation

	#	#	#	**
Average Molecular Weight a	836	846	841	817
Ash			0.22%	0.21%
Insolubles:				
benzene			0.0%	by weight
toluene			0.1%	
pentane			49.2%	
<u>Ultimate</u>				
carbon			82.32%	82.63%
hydrogen			10.43%	10.35%
nitrogen			1.14%	1.07%
oxygen (by expt.)			1.26%	1.17%
sulphur			5.38%	5.49%
H/C (atomic ratio)			1.52%	1.50%

Ash Analysis

SiO *	188 mg/kg pitch
2	
Al O	97
2 3	
Fe O	12
2 3	
Mn O	0
3 4	
CaO	6
MgO	5
Na O	144
2	
K O	6
2	
V O	440
2 5	
NiO	154
ZnO	8

*

Silica analysis was accomplished by NaOH digestion of the pitch sample in a Parr bomb, followed by spectrophotometric determination of silica content.

III.2.1.1 Average Molecular Weight

ASTM D224 was followed for the determination of average molecular weight. The determination of molecular weight was also carried out by vapour pressure osmometry.

III.2.1.2 Ash Content

ASTM D3174 was followed for the determination of ash content. In this method 5 g of pitch was weighed in a crucible and heated in a muffle furnace at 700 °C for four (4) hours. The ash was cooled and weighed.

The determination of metals in the ash was accomplished by standard atomic absorption technique. The ash sample was digested in an aquaregia in a Parr Bomb and the resulting solution analyzed.

III.2.1.3 Insolubles

(a) Benzene Insolubles (soxhlet extraction)

1 gram of sample was weighed into the thimble and extracted in a soxhlet apparatus with 200 ml of benzene for approximately 3 hours until the solution around the thimble was consistently clear. The weight of sample left after extraction was calculated.

Freezing Point Depression Method; ASTM D224

** VPO Method (Hitachi-Perkin Elmer instrument)

*** Cold Lake Vacuum Bottom Pitch dated 19.1.1984 was supplied by Dr. M. Ternan, ERL/CANMET

(b) Insolubles in Other Solvents

A weighed quantity of pitch was dissolved in about 100 fold excess of solvents, filtered through a filter paper, washed in increments of solvents and dried at room temperature to a constant weight. The percentage of insolubles were calculated from the total residues on filter paper.

(c) CHNO Analysis

The CHN analysis of pitch was performed using Perkin Elmer Elemental Analyzer, model 240B. In this method a known weight of sample was combusted at 1,000 °C in the presence of oxygen. The gases produced were passed through oxidation furnace and then through the reduction furnace. The resulting gases CO_2 , H_2O and N_2 were analyzed chromatographically. The NBS standards: acetanilide, phenacetin and cyclohexane, 2,4 dinitrophenyl hydrazine were used in the calibration of the instruments.

The apparatus was modified, as required in Perkin Elmer instrument manual, for oxygen analysis.

^a

ASTM D3174-73

^{*}

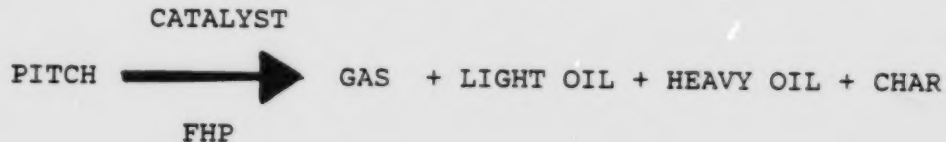
this procedure was used to avoid exposure to benzene.

(d) Sulfur Analysis - Oxygen Flask Method

The sulfur content in the pitch was determined by the method of reference (84). In this method the sample of pitch was combusted in a closed flask filled with oxygen. Using hydrogen peroxide as absorbent, all sulfur was converted to sulfate. The sulfate was then titrated at pH 3 in alcohol-water mixed solvent with barium perchlorate as titrant using thorin-methylene blue mixed indicator.

III.2.2 Analysis of FHP Products

Typical flash hydropyrolysis of pitch produces a wide range of gaseous and liquid products:



The FHP products were passed, see figure 21, through stainless steel coiled trap at -50°C . The coiled trap at -50°C was prepared by cooling about a litre of acetone in thermos flask. Liquid nitrogen from another thermos was gradually added on to the solvent under constant stirring until the desired temperature of -50°C was attained. The bath was then brought to the line and securely fastened with the trap immersed. The mouth of the thermos was insulated by covering with quartz glass wool. Such a bath was found to hold the trap at this temperature for greater than 1 hour -

much beyond our experimental requirement (~30 minutes). The condensable materials were thus held in the trap and gaseous materials were collected for 20 minutes into evacuated sampling cylinder. The gaseous product which mainly consisted of C₁ to C₅ hydrocarbons were analyzed by gas chromatography. Hewlett-Packard gas chromatograph model 5830 (FID) with a 10 ft X 0.125" stainless steel column packed with activated alumina coated with 17% ¹BB oxydipropionitrile 100/120 mesh was used for the analyses of C₁ - C₅ hydrocarbon gases. A small quantity of CO, CO₂, NH₃ and H₂S that may be produced in the reaction process were not analyzed.

The liquid products left in the trap at -50 °C were separated into two fractions: the "light oil" fraction and "heavy oil" fractions as follows: The trap was heated to 100 °C and the hydrogen flow diverted to a trap filled with Fisher Activated Carbon 6-14 mesh, where the "light oil" fractions were adsorbed. The activated carbon trap was then desorbed with carbon disulfide and analyzed by gas chromatography (FID) using 20 ft X 0.125" OD 10% FFAP 100/120 mesh. The light fraction so analyzed was found to contain BTX type liquid. This separation technique was validated by analysis of standard mixture of BTX and hydrocarbon gases. The recoveries were greater than 95%.

The remaining products in the trap arbitrarily defined as "heavy oil" was then extracted with carbon disulfide. The solvent was evaporated at 60°C, and the contents were weighed. The elemental analysis for % carbon was then performed.

The gas chromatographic conditions for the analyses of light liquids and hydrocarbon gases CH_4 , C_2H_4 , C_2H_6 , C_3H_8 , C_4 's and C_5 's are given in table 4. Whereas the conditions for the analyses of heavy liquids on char are given in table 5.

Table 4

Conditions for GC Analyses, Light Liquid and
Hydrocarbon Gases

Condition	Light Liquid	Hydrocarbon Gases [*]
Column	0.25" stainless steel tubing, 20 feet long, 10% FFAP on 100/120 mesh supelcoport.	0.25" Stainless steel tubing, 10 feet long, 17% ~~PP~~ "-oxidipropio- nitrite on activated alumina 100/120 mesh.
Carrier gas	N 2	N 2
Flow rate	25 cc/min	22 cc/min
Detector	FID °	FID °
Detector temperature	250 °C	150 °C
Injector temperature	250 °C	50 °C
Transfer line temperature	--	30 °C
Temperature programing rate	--	--
Column temperature	100 °C	50 °C
Sample size	1-3 μ l	0.500 c.c.

*

the conditions varied in some experiments, however such
variation did not affect large changes in retention time.

Table 5

Conditions for GC Analyses, Heavy Liquid
(by simulated distillation) and char by
combustion

Condition	Heavy Liquid (by simulated distillation)	CO Analyses from Char residue
Column	0.25" stainless steel 20 inch 10% UCW 982 PAW 80/100 mesh	0.25" stainless steel 6' long Spercarb 80/100 mesh
Carrier gas	N ₂	He
Flow rate	26 cc/min	20 cc/min
Detector	FID	TCD
Detector temp.	350 °C	80 °C
Injector temp.	350 °C	30 °C
Transfer line temp.	--	30 °C
Temp. Programming rate	10 °/min	--
Column temperature	40-350 °C	80 °C
Sample size	1-3 µl	combustion residue

III.2.2.1 Gaseous Products

The hydrocarbon gases produced in the FHP experiments typically included methane, ethane, ethene, propane, propene, and butanes. Under the gas chromatographic conditions of tabel 4.the peaks of the gaseous hydrocarbons in most cases

were well separated. The gas chromatograms of two experimental runs typical in catalytic FHP of pitch observed in this investigation are given in figures 25 and 26. Standard gaseous hydrocarbons from Matheson company were used in the identification (by retention time) and quantification of the peaks.

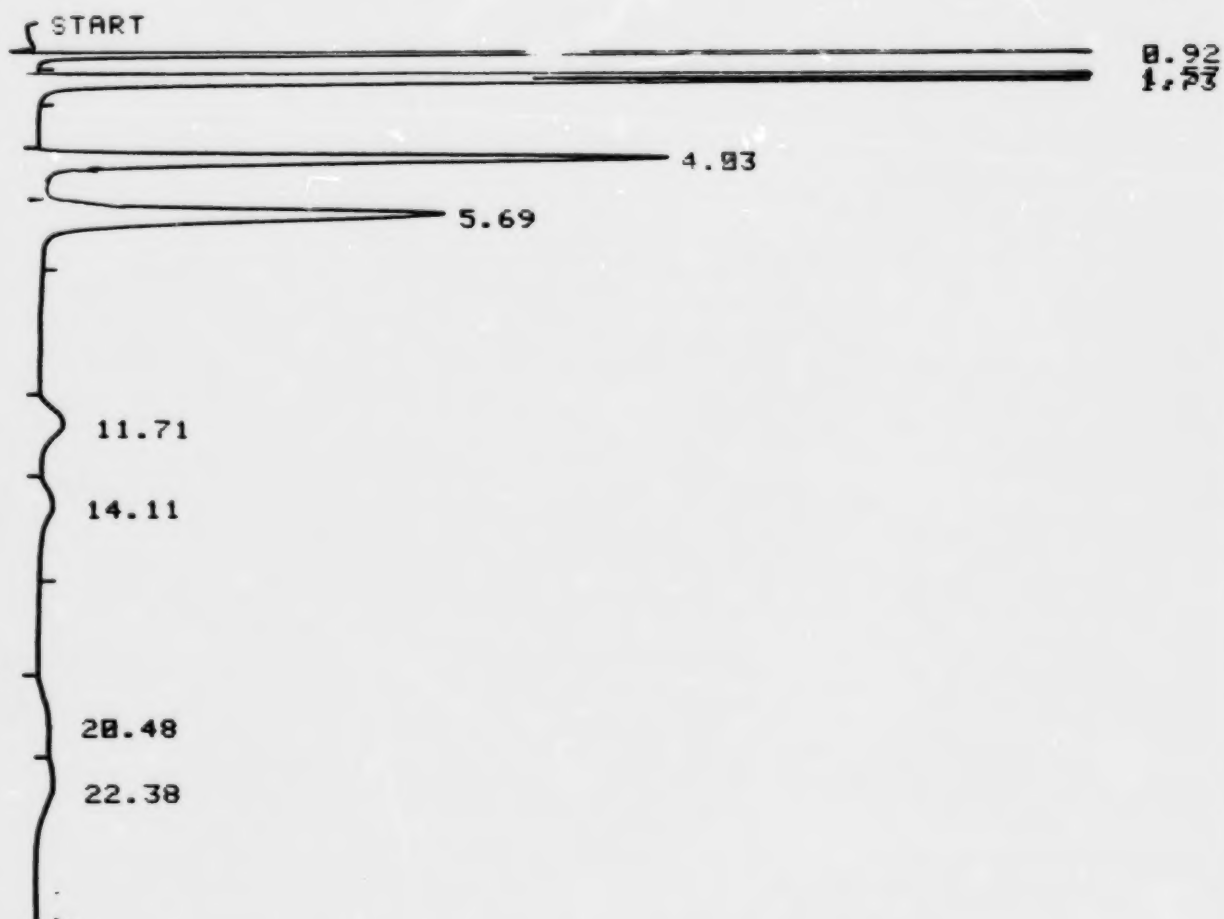


Figure 25: Typical Chromatogram of
Gaseous Hydrocarbons C₁-C₅
in FHP Run # 77
catalyzed by ZnCl₂

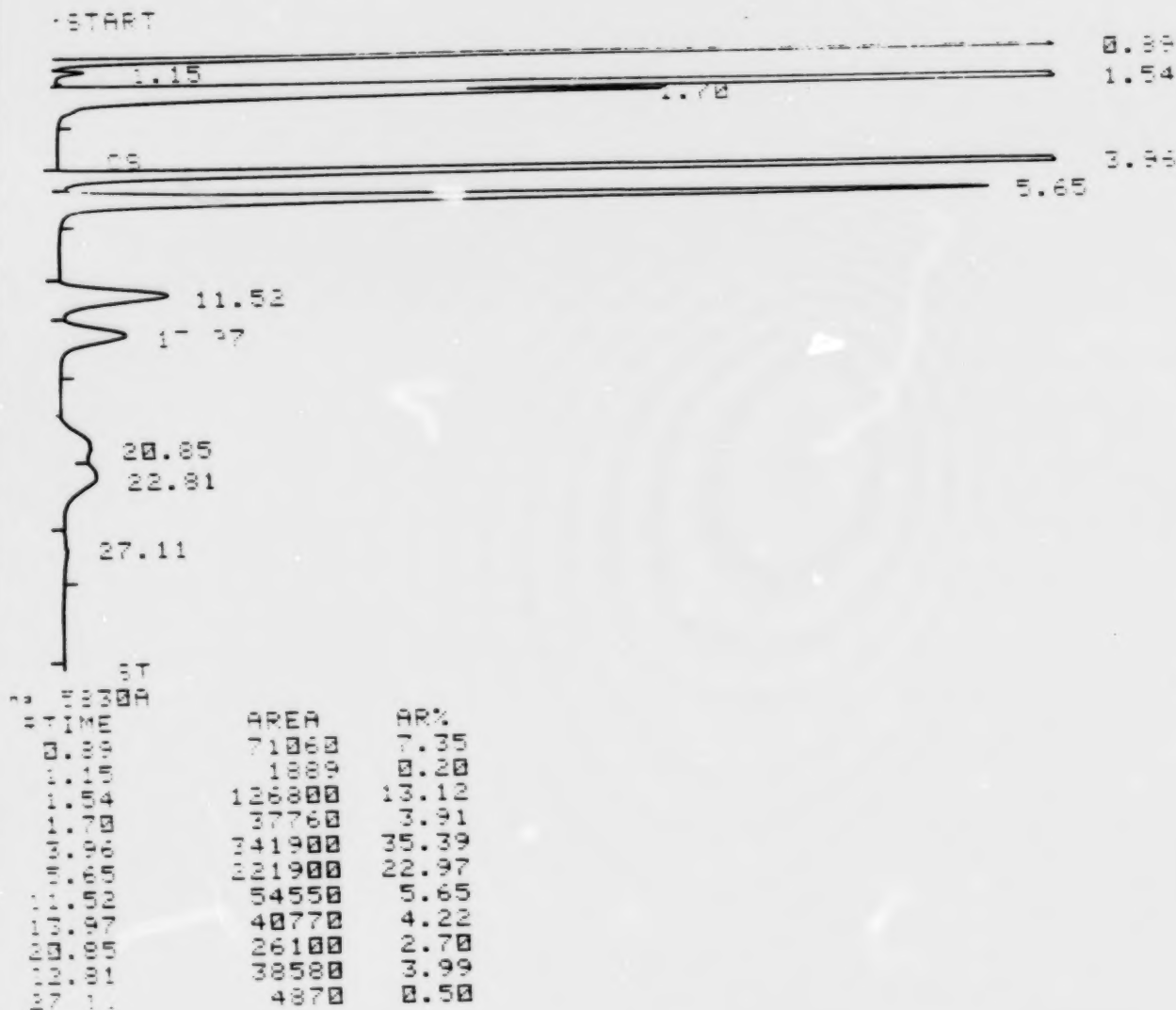


Figure 26: Typical Chromatogram of
Gaseous Hydrocarbons C -C
in FHP Run # 2 1 5
catalyzed by sodium Nitrate
on SiO₂

III.2.2.2 Light Hydrocarbon Liquids

The low boiling hydrocarbons produced in the FHP were predominantly benzene, toluene, xylenes (BTX) and minor components of other substituted products. When the liquid products could not be identified an average FID response for BTX was tacitly assumed for quantitative analyses of such products. Typical chromatograms illustrating the separation under the GC conditions of table 4 are given in figures 27 and 28.

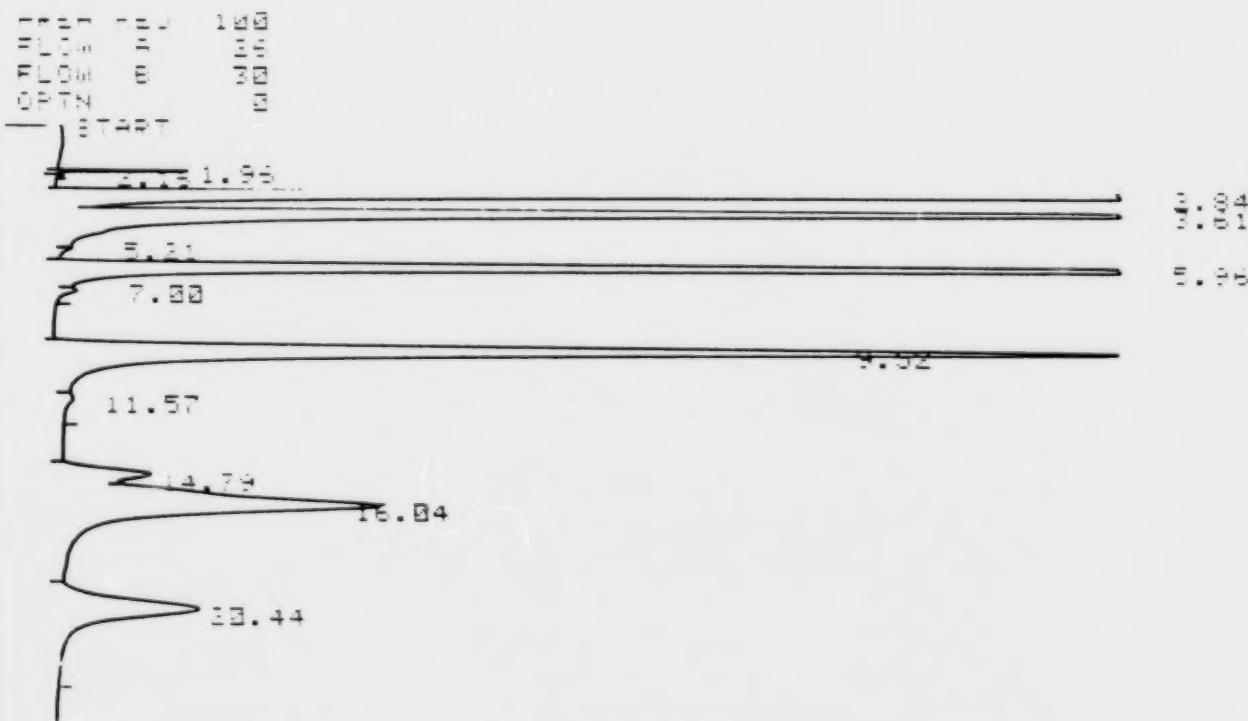


Figure 27: The chromatogram of Standard BTX under the GC conditions of table 4.

III.2.2.3 Heavier Hydrocarbon Liquids by GC Distillation,
ASTM 2887

The heavier liquid products separated by the procedure described above were much more complex than lighter liquids and gaseous hydrocarbons. It was therefore not possible, as expected, to resolve the individual components by any of the available analytical techniques.

Simulated distillation was performed by gas chromatography according to ASTM D 2887, ref. (85). The method is based on the principle that the chromatographic column separates the mixture strictly according to boiling point. The molecular shape and size or polarity do not affect the separation. The following procedure was followed:

The calibration standard sample # 5080-8716- a mixture containing hydrocarbons: C₅ to C₄₀ for use with ASTM D 2887 from Hewlett-Packard of Canada was used in the calibrations. The gas chromatograph in use was H/P 5830A with dual FID fitted with H/P integrator 18850A with automatic integration capabilities. The column used for simulated distillation was 0.25 X 20 inches stainless steel, 10% UC-W982 on 80/100 mesh chromosorb P-AW. The dual columns were attached to the FID with the 0.030 inch jets. The operating conditions of the GC were as follows:

Inject port	350 °C	Temp. 2: 350 °C
FID port	350 °C	Time 2:10 min
Initial oven temp.	40 °C	Flow A: 26 mL/min
Time 1	0.0 min	Flow B: 26 mL/min
Rate	10.0 °C/min	Signal: (A - B)

The sample of high boiling material was mixed with carbon disulfide.

2 μ l of the standard was injected on the column A in temperature program mode of GC. It was ensured that the chromatographic signal returned to a constant base line at the end of the run. The temperature programming was capable of uniformly heating the chromatographic column up to maximum temperature used. Thus any cold spots on the column were avoided. Blank runs were taken with the solvent. Several hours of conditioning was carried out to avoid extraneous peaks from septum bleed whenever new septums were installed. The chromatograms were corrected for blanks. The area under the chromatogram was integrated continuously. The plot of boiling point versus retention time is shown in figure 29. The plot of figure 29 was constructed from average retention time of three chromatograms as shown in figure 30. The retention times were highly reproducible (± 0.3). The plot of retention time vs. carbon number is given in Figure 31.

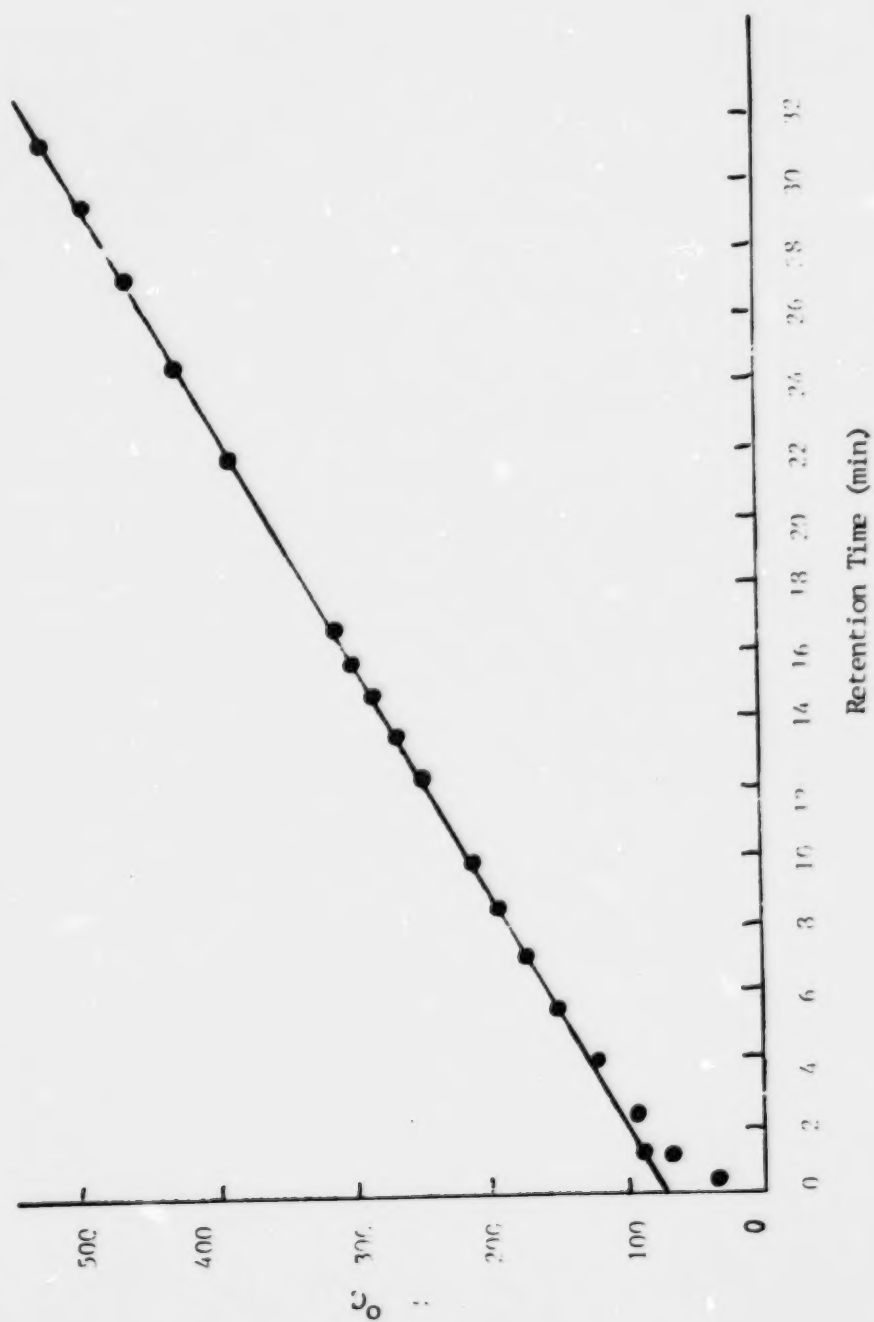


Figure 22 Plot of temperature vs Retention time

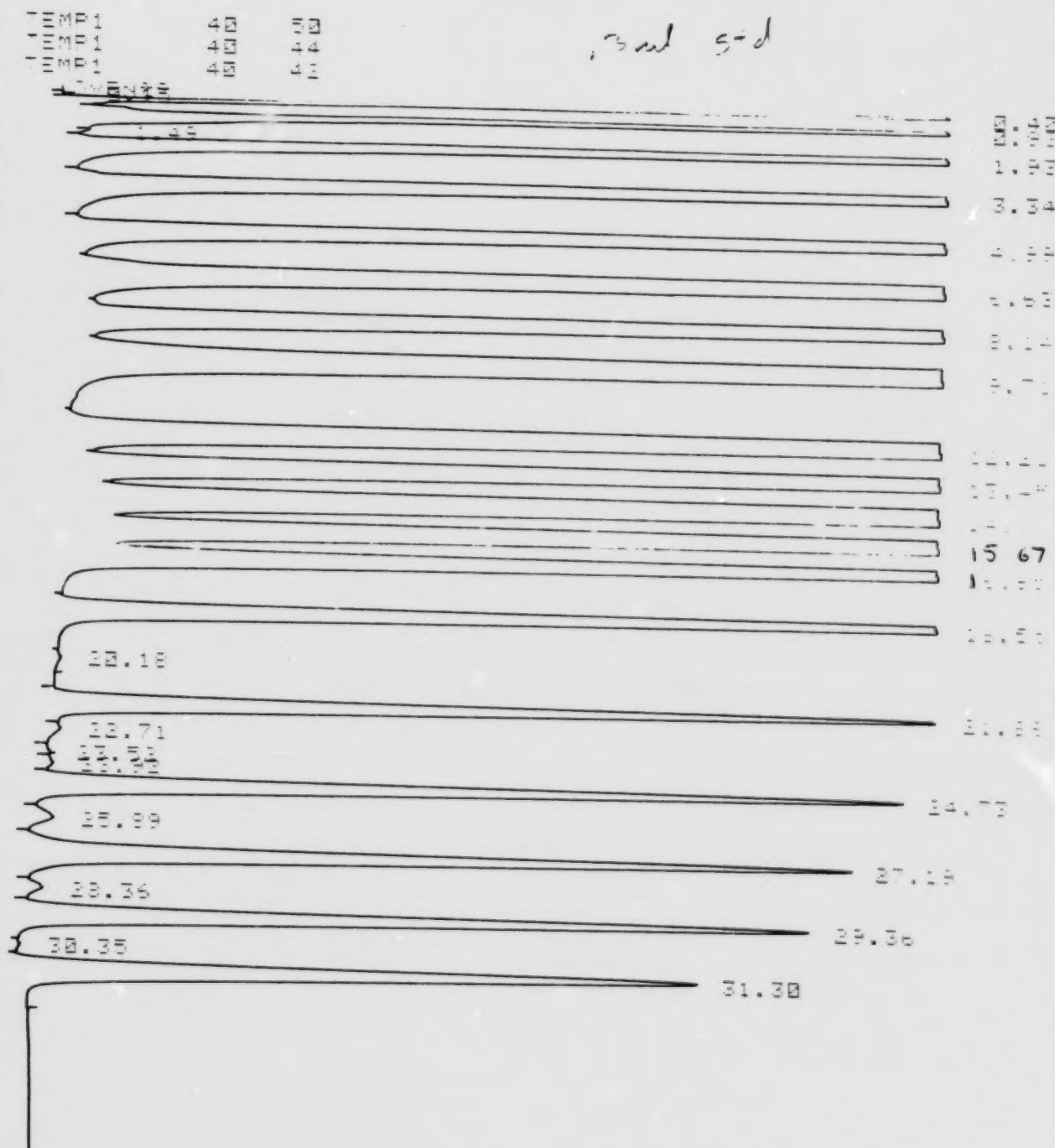


FIGURE: 30 Chromatogram of the
Standard used for the
Simulated Distillation

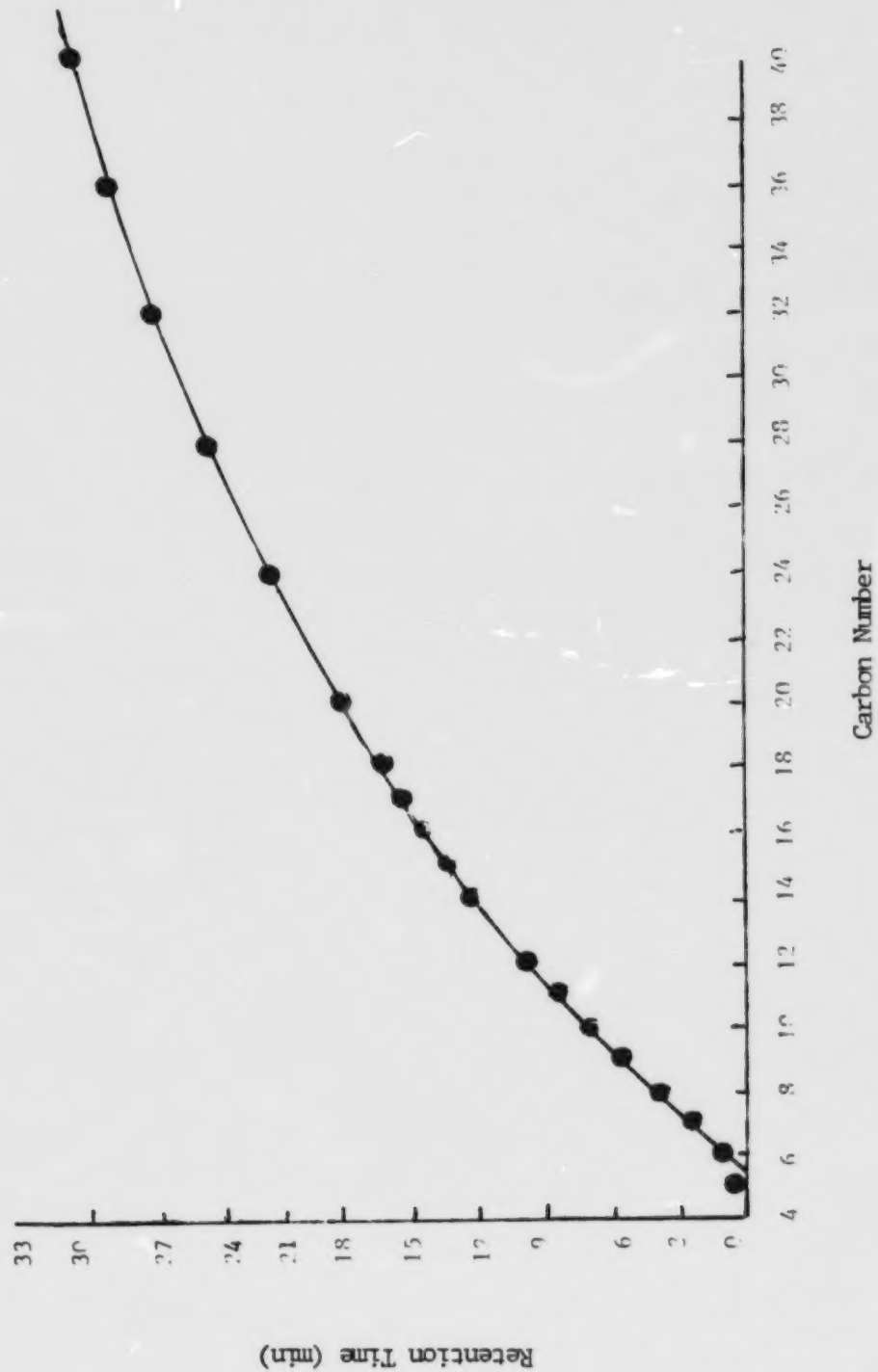


FIGURE: 31 Plot of Retention Time vs Carbon Number

As shown in figure 29 an excellent correlation was formed between boiling point and retention time for components boiling above 80 °C. From the slope and intercept the boiling point could be calculated:

$$BP = 75 + 14.467 X$$

Where BP is the normal boiling point in °C and X is the retention time.

For the components boiling at or below 80 °C a different correlation was found:

$$BP = 35 + 25 X$$

In the preparation of histograms the low boiling products were analyzed separately and were found predominantly BTX liquid.

The liquid product chromatogram was divided into a convenient equal size intervals and the integrated peak area was counted within each interval. The area due to base line shift was determined by running a blank and in each interval the appropriate correction was made.

The simulated distillation correlation was checked by injecting a mixture of benzene, toluene, naphthalene, phenanthrene and chrysene in carbon disulfide into a gas chromatograph and noting the retention time. The calculated boiling point from the retention time were in excellent agreement to the actual boiling point of these pure compounds.

III.2.2.4 Analysis of Char Residue

The char produced in the FHP was analyzed by combusting the residual at 800 °C with oxygen. The carbon dioxide produced was measured by gas chromatographic technique using T.C. detector. The carbon in the char was thus determined and added to other products to construct a material balance on carbon. A calibration curve was constructed using NBS standard and pitch (% C analyzed on P-E instrument) as shown in Figure 31. From the area of the carbon dioxide peak produced from the combustion of char the weight of carbon in char was deduced from the plot of figure 32.

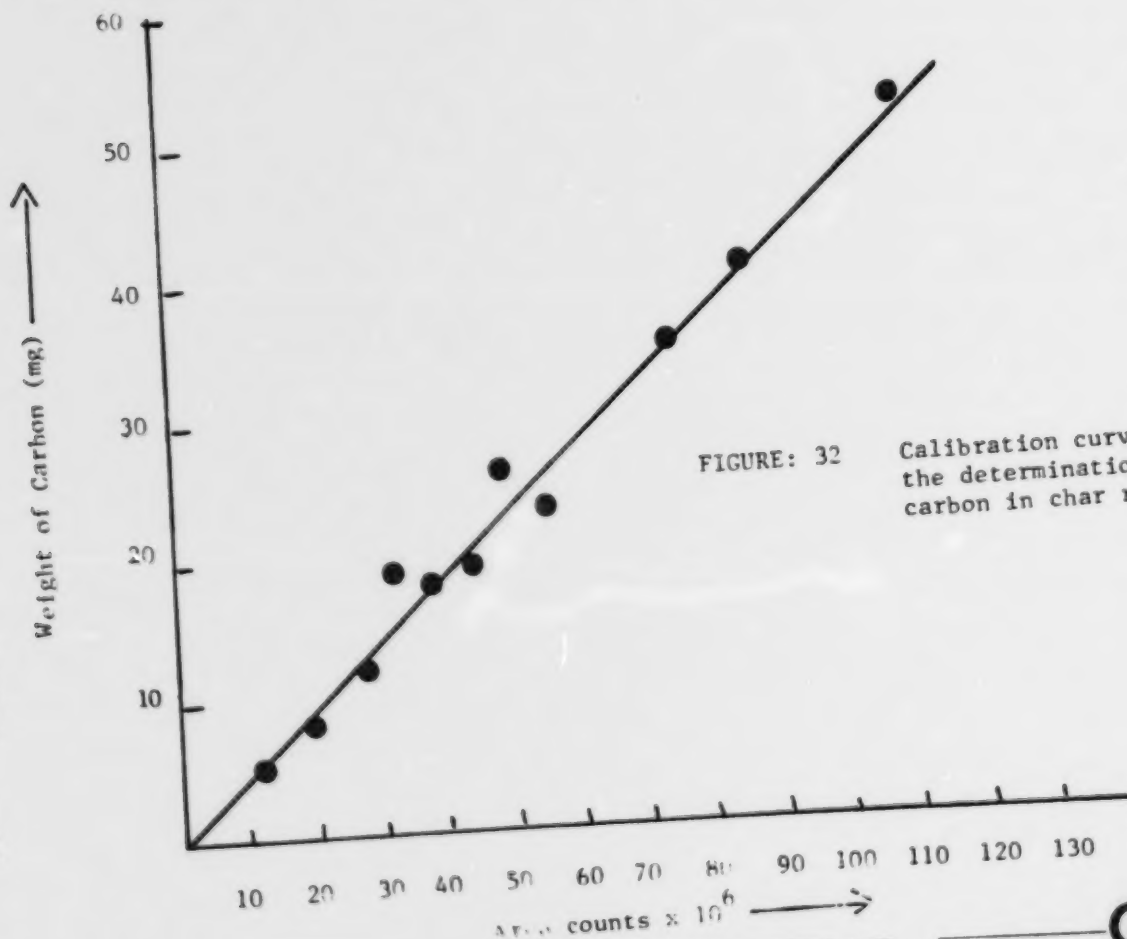


FIGURE: 32 Calibration curve for the determination of carbon in char residue.

IV.0 PREPARATION OF CATALYSTS

An effective catalyst that will selectively crack the PNA structure to maximize the liquid yields was needed. Several catalysts were screened in the Flash Hydropyrolysis of Cold Lake Pitch. Some of the catalysts were purchased directly from the supplier and required no further preparation.

A summary of the catalysts and their corresponding suppliers are given in table 6. The method of preparation was as follows:

IV.1 Chlorides

The solid chloride powders were purchased: KCl , CaCl_2 , AlCl_3 , and ground to - 200 mesh, and used as catalysts.

IV.2 ZnCl_2

Work at the University of Utah has shown that up to 70% conversion of coal to combined liquid and gas yields can be achieved under mild FHP conditions (500°C and 1800 psig H_2) when ZnCl_2 is used as a catalyst with Kentucky bituminous coals at lower temperature and pressure, e.g. $482\text{--}510^\circ\text{C}$ and 1000 psig H_2 pressure. This catalyst was used as received basis.

IV.3 $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$

This catalyst was used as received basis.

IV.4 ZnO-Cr₂O₃

141.0 g of Zn(NO₃)₂ · 6H₂O and 60 g of Cr(NO₃)₃ · 9H₂O were placed in a 800 ml beaker and dissolved in a minimum amount of water (~100 ml). Zinc and chromium hydroxides were then precipitated by adding an excess of aqueous ammonia. The precipitate was filtered off with suction. Washed with NH₄OH then dried in the air until damp. The moist precipitate was heated in an oven at 120 °C for 24 hours then ground to 200 mesh.

It should be noted that if the catalyst is not precipitated all at once, then it can not be assured that the required ratio of 4:1 Zn:Cr is maintained. However, this is difficult to do with large quantities of zinc and chromium nitrates. In this particular preparation it took two filtrations to obtain a clear mother liquor. Both precipitates were collected and stored separately. A 64% yield was obtained.

IV.5 Binary Oxides

SiO₂ was impregnated with aqueous solutions of sodium nitrate, magnesium nitrate, aluminum nitrate and ortho phosphoric acid in such a manner to obtain a 1:10 ratio of third row element to silicon. The required mass of nitrate was dissolved in 100 ml of water in an 800 ml beaker. The solution was stirred with a magnetic stir bar and 97.3 g of

SiO₂ was added slowly with continuous stirring. The SiO₂ was washed into solution periodically. Most of the water was boiled off on a hot plate with continuous stirring. The damp catalyst was transferred to a crucible and heated at 110 °C for 10 hours then calcinated at 500 °C for 6 hours. The dry catalyst was ground and stored for FHP experiments. Samples of all the catalysts were supplied to Scientific Authority.

Table 6
Sources of Catalyst Materials

CATALYST	MATERIALS	SOURCE	CAT #	GRADE
KCl	-	Van Waters and Rogers	JT3046-1	OSP
CaCl ₂ .2H ₂ O	-	BDH	B10070-34	ANAL "R"
AlCl ₃ .6H ₂ O	-	BDH	B27024-34	BDH Assured
SnCl ₄	-	BDH	B30248-70	BDH Assured
ZnCl ₂	-	Caledon	9120-1-70	Reagent
FeSO ₄ .7H ₂ O		BDH	B10112-34	ANAL "R"
ZnO-Cr ₂ O ₃	Zn(NO ₃) ₂ .6H ₂ O	BDH	B10335-34	ANAL "R"
	Cr(NO ₃) ₃ .9H ₂ O	BDH	B27755-34	
	NH ₄ OH	Baker		ANAL "R"
Binary	SiO ₂	BDH	B30057-34	ANAL "R"
Oxides	Al(NO ₃) ₃ .9H ₂ O	BDH	Bi0300-34	ANAL "R"
	NaNO ₃	BDH	Bi0255-34	ANAL "R"
	Mg(NO ₃) ₂ .6H ₂ O	BDH	Bi0309-34	ANAL "R"
	H ₃ PO ₄	BDH	Bi0173-74	ANAL "R"

V RESULTS AND DISCUSSION

V.I Results of Non-Catalytic Experiments

To begin with FHP experiments were carried out without catalysts. The results are given in tables 7 and 8. The recoveries were found to be greater than 90% and the char residue >30%. Systematic effort of reproducing a heating rate and final temperature were hampered by the heating technique employed, i.e. bank of batteries and solenoid system. Whenever predetermined heating rate, final temperature fluctuated to unacceptable levels runs were terminated. Results reported for reproducibility are those which randomly reproduce the predetermined conditions or are close for comparison.

V.2 Results of ZnCl₂ Catalyzed Experiments

The results of some preliminary experiments performed for repeatability and developing base conditions are given in tables 9 and 10. These results show a definite catalytic effect that the formation of char has been significantly reduced. Typical experimental results are given in tables 12 to 16 including a run without catalyst. Data were normalized on carbon assuming no loss of products. The effect of significant variables in the conversion experiments were studied over a range given in table 11. These variables were optimized for desirable product

selectivity, i.e. lower gases, char residue and high yields of liquid distillates.

Table 11

Range of process variables studied

Temperature:	300 - 1,100 °C
Heating Range:	110 - 330 °C/s
H Pressure:	250 - 1,400 psig
Vapour residence time:	3.5 - 11 sec
Catalyst/pitch weight ratio:	0.4 - 2

The effect of process variables on product selectivity are given in tables 17 to 22 and are plotted in figures 33 to 38.

The temperature versus time profile curves from which heating rates were calculated in these experiments are given in figures 39 to 50.

Effect of Temperature

Figure 33 shows the effect of temperature on the product yield. The yield of gaseous hydrocarbons (C₁ to C₄) produced in the FHP of pitch increases dominantly with temperature, whereas the char formation is only slightly affected after 500 °C. The BTX also increases with temperature. The effect, however, is small in comparison to gaseous hydrocarbons. It

would appear that BTX and gaseous product formation is accompanied by lowering in heavy liquid products.

Effect of Heating Rate

As shown in figure 34, heating rate produces desirable effects at $\sim 230^{\circ}\text{C/s}$, then the heavy liquid products decrease with the formation of increased gases and char.

Effect of Residence Time and Hydrogen Pressure

The effect of residence time for which the sample is maintained at the final temperature was found to have a pronounced effect. As shown in figure 35 and 36 both the char formation and the hydrocarbon gases were lowered and then increased with longer residence time. At the longer residence time, the secondary reactions leading to high char become increasingly important. The sharp drop in high boiling distillate is also observed in the region of residence time >4 sec indicating that there is little advantage in holding the sample at the temperature for greater than 4 seconds.

The effect of total hydrogen pressure was studied in the range 250-1,400 psig. The formation of high boiling distillates decreased slightly, whereas the char formation and light boiling liquids were unaffected in the pressure range 250-1,000 psig. At further increase in pressure to 1,400 psig, the char formation apparently increased within

the experimental error of measurements. This increase was accompanied with increase in light boiling components. In this regime of pressure an important observation is the decrease in the total gas formation and increase in light boiling component of the products.

Effect of Catalyst/Pitch Ratio

Figure 37 shows the effect of the catalyst to pitch ratio on the product distribution. The major effect is the decrease of the heavy distillate with an increase of all other products.

Heavy Liquid Products

Typical simulated distillation of liquid products from experimental runs, relating % boiling off vs. temperature and their corresponding histograms are given in figures 51 to 64. The typical simulated distillation of the pitch samples and the histogram of the products are given in figures 65 and 66 respectively for comparison. The results indicate that in zinc chloride catalyzed reactions, about 90% of the pitch is converted to products boiling off below 440°C , whereas the pitch % boiling off at this temperature is about a maximum of 15%. A portion of the unconverted pitch would contaminate the collected heavy liquid products. In calculating the weight of heavy liquids from experimental data, a pertinent correction for unconverted pitch, though small, was not

applied in the plots. Furthermore, the char remaining in the reactor may have contamination from the unvolatilized pitch, if any. Despite these sources of contamination from the unconverted pitch a mass balance on carbon will not be affected.

Light Products

Products other than char and heavy liquid were gases and light boiling liquid. The typical gaseous products included methane, ethane, propane, butane, pentane and ethene, propene with traces of pentene. Typical distribution of the gaseous hydrocarbon products are given in the histogram of the heavy liquid products. The methane, C₂'s and C₃'s are the dominant component of the product, whereas C₄'s and C₅'s are only in small amounts. The effect of heating rates on the selectivity of gaseous hydrocarbons are plotted in figure 38. In the regime of temperatures 300-700 °C, the production of methane and ethane increases dominantly whereas propane, propene and ethene production decreases significantly between 500 and 700 °C. The other gaseous composition is not significantly changed in this region. The effect of heating rate as shown in figure 38 is similar to temperature effects in that the methane and ethane in the total make-up of the gaseous hydrocarbon are found to be dominantly affected by the heating rate. Effect on other products is small.

The low boiling liquid primarily was BTX and were collected

by desorbing the charcoal trap in carbon disulfide. These represented a very small component of the total liquid products make-up and are displayed in the histogram figures as low boiling liquids.

The theme of this investigation was to study the catalytic FHP of raw cold lake pitch and optimize the process variable such as pressure, temperature, heating rate and residence time for conversion of the pitch to yield: liquid and SNG products with the minimum formation of char. The study on ZnCl_2 catalyzed FHP has demonstrated that suitable parameters in achieving these objectives are: temperature 520-560 °C, heating rate 210-240 °C/sec, residence time 3.5-4.0 seconds and the pressure of 1,000 psig.

V.3 - V.11 Results of Other Catalytic Experiments

FHP experiments carried out in the presence of other catalysts are given in section V.3 to V.11. The simulated distillation and histogram of the liquid products have been included. As can be seen the impregnated catalysts are found to be very active - despite the low catalyst to pitch ratio used ($< 0.5\text{m/m}$). These catalysts selectively produce undesirable gases.

Figure 109 summarizes the main product distribution in the FHP of pitch catalyzed by various catalysts used in this investigation. The uncatalyzed reaction is also shown for

comparison. The results of other catalysts i.e. KCl and CaCl₂ (not shown in figure 109) are given in tables 37 and 38. Zinc chloride emerges as the best among the catalysts examined. It yields lower char values, lower gaseous product and desirable boiling range distillate.

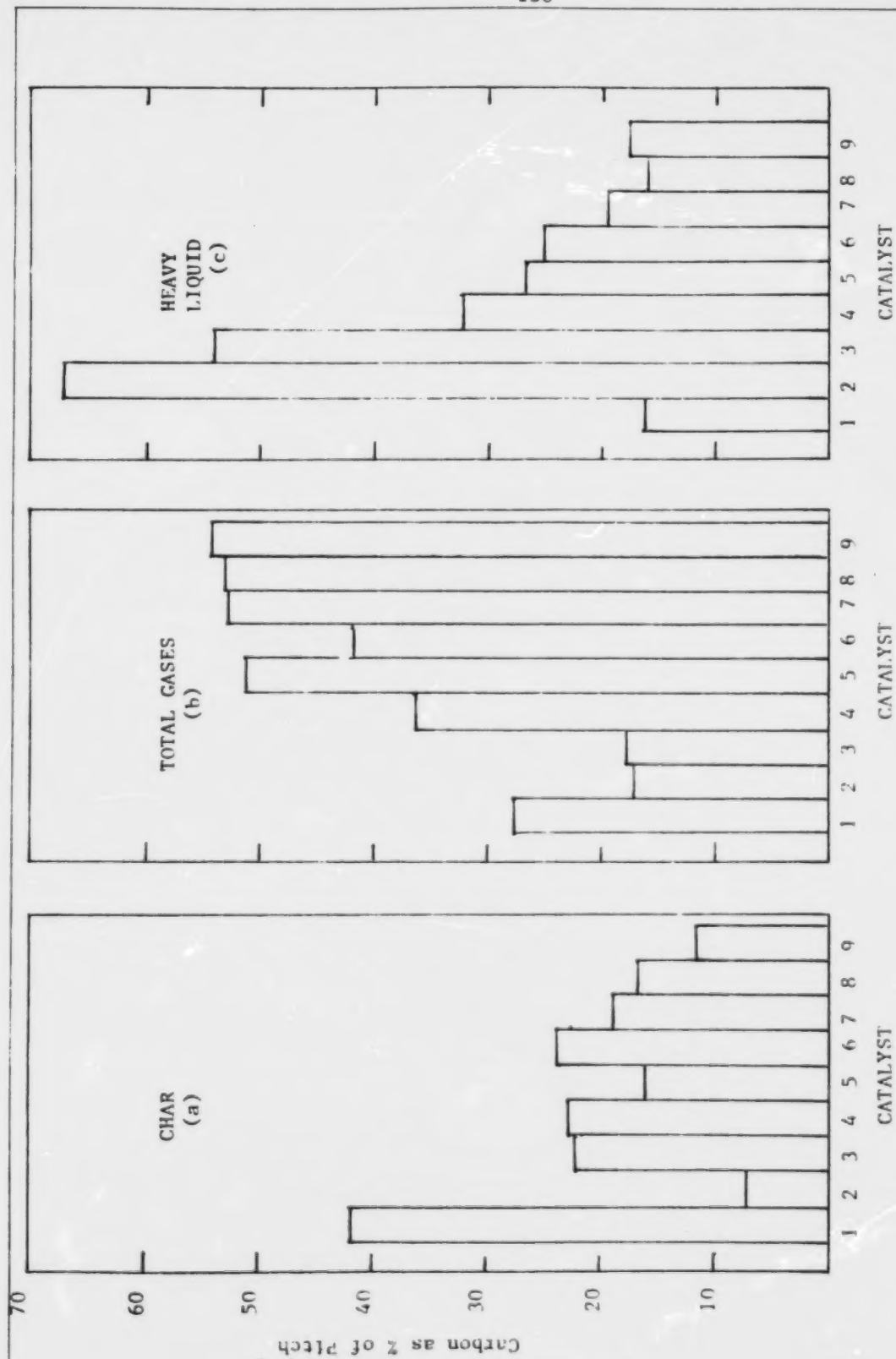


FIGURE 109: Summary of the main product distribution (% C normalized for comparison) under optimum conditions. Heating rate = $230 - 240^\circ\text{C}/\text{sec.}$, Maximum temperature = $550 - 582^\circ\text{C}$, hydrogen pressure = 1000 psi, residence time = 3.95 s
Catalyst, 1. None, 2. ZnCl_2 , 3. SnCl_4 , 4. Al-SiO_2 , 5. Na-SiO_2 , 6. Fe-SiO_2 , 7. P-SiO_2 , 8. ZnO_2 , 9. ZnO_2

Table 7

Results of Non-Catalytic Experiments

Run No.	Pitch A 1	Pitch A 2	Pitch A 3	Pitch O 2
Catalyst type	none	none	none	none
Catalyst/pitch ratio m/m	0.0	0.0	0.0	0.0
Heating rate °C/sec	237	237	190	237
Maximum temperature °C	523	523	475	582
H ₂ pressure psi	1,000	1,000	1,000	1,000
resident time sec	3.95	3.95	3.95	3.95
mass pitch mg total	57	58	58	90
mass pitch mg C	46.9	47.7	47.7	74.1
<u>m %C of Pitch</u>				
C ₁	3.3	5.2	1.9	8.5
C ₂ 's	5.5	8.1	3.6	11.5
C ₃ 's	6.3	5.8	4.2	5.7
C ₄ 's	1.4	1.7	2.9	0.8
C ₅ 's	1.5	1.6	2.1	1.1
Other	-	-	-	-
Total gas	18.0	22.4	14.7	27.6
<u>Liquids</u>				
Light Distillate	4.9	4.1	6.9	8.1
Heavy Distillate	35.0	29.4	-	16.3
Residue	31.6	38.1	-	41.6
TOTAL	89.5	94.0		93.6

Table 8
Results of Non-Catalytic Experiments

Run No.	Pitch 16	Pitch 17	Pitch 18
Catalyst type	none	none	none
Catalyst/pitch ratio m/m	0.0	0.0	0.0
Heating rate °C/sec	261	261	261
Maximum temperature °C	689	606	594
H ₂ pressure psi	250	250	250
resident time sec	3.95	3.95	3.95
mass pitch mg total	90	98	95
mass pitch mg C	74.1	80.7	78.2
<u>m %C of Pitch</u>			
C	4.6	2.9	3.2
C ₁ 's	9.9	6.9	7.5
C ₂ 's	6.4	5.3	5.8
C ₃ 's	0.4	0.5	0.7
C ₄ 's	4.6	4.3	4.2
C ₅	-	-	-
Other	-	-	-
Total gas	25.9	19.9	21.4
<u>Liquids</u>			
Light Distillate	7.7	6.9	7.5
Heavy Distillate	25.4	26.5	25.9
Residue	37.6	40.3	35.6
TOTAL	96.6	93.6	90.4

Table 9
Experiments For Comparison and
Developing Base Conditions

Run No.	Zn57	Zn59	Zn60	Zn64
Catalyst type	ZnCl ₂	ZnCl ₂	ZnCl ₂	ZnCl ₂
Catalyst/pitch ratio m/m	1.04	1.07	1.03	1.84
Heating rate °C/sec	249	261	237	274
Maximum temperature °C	535	594	558	594
H ₂ pressure psi	1,000	1,000	1,000	1,000
resident time sec	3.65	3.65	2.4	3.65
mass pitch mg total	91	92	72	57
mass pitch mg C	74.6	75.7	59.3	46.9
<u>m %C of pitch</u>				
C ₁	10.6	14.8	6.2	13.3
C ₂ 's	12.0	13.5	8.3	15.0
C ₃ 's	3.2	2.6	6.7	3.1
C ₄ 's	0.4	0.2	1.2	0.2
C ₅ 's	1.1	0.5	2.3	0.1
Other	-	-	-	-
Total gas	27.3	31.6	24.7	31.7
<u>Liquids</u>				
Light Distillate	16.7	13.2	14.5	14.9
Heavy Distillate	45.0	45.2	43.4	41.5
Residue	11.0	10.0*	-	11.9*
TOTAL	100.0	100.0	-	100.0

* residue by difference

Table 10
Experiments For Comparison and
Developing Base Conditions

Run No.	Zn74	Zn75	Zn76
Catalyst type	ZnCl ₂	ZnCl ₂	ZnCl ₂
Catalyst/pitch ratio m/m	0.97	0.99	1.19
Heating rate °C/sec	238	238	238
Maximum temperature °C	535	535	559
H ₂ pressure psi	250	250	50
resident time sec	3.95	3.95	1.98
mass pitch mg total	100	101	108
mass pitch mg C	82.3	83.1	88.9
<u>m %C of Pitch</u>			
C ₁	2.6	2.1	0.6
C ₂ 's	4.3	3.8	1.2
C ₃ 's	4.4	3.3	1.3
C ₄ 's	0.6	0.8	0.5
C ₅ 's	3.1	3.5	1.1
Other	-	-	-
Total gas	15.0	13.5	4.7
<u>Liquids</u>			
Light Distillate	6.4	8.4	2.9
Heavy Distillate	70.9*	74.6	-
Residue	7.7	3.5	7.8
<u>TOTAL</u>			

* by difference

Table 12

Typical experimental run without catalyst

Run # Pitch O
 Final temperature = 582 °C
 Heating rate = 237 °C/sec
 Hydrogen pressure = 1000 psig
 residence time = 3.95 seconds

Product	mg C	% C of starting pitch	% C normalized
Methane	6.3	8.5	9.1
C 's 2	8.5	11.5	12.3
C 's 3	4.2	5.7	6.1
C 's 4	0.6	0.8	0.9
C 's 5	0.8	1.1	1.2
Total gas	20.4	27.5	29.4%
BTX	6.0	8.1	8.7
C+ 8	12.1	16.3	17.5
Char residue	30.8	41.6	44.5
Totals	69.3	93.6	100.3

Table 13

Typical experimental run under reaction conditions

Run # Zn80

Final temperature = 511 °C

Heating rate = 237 °C/sec

Hydrogen pressure = 1000 psig

residence time = 3.95 seconds

catalyst/pitch ratio = 2.1 m/m

Product	mg C	% C of starting pitch	% C normalized
Methane	1.8	3.8	4.5
C ₂ 's	2.6	5.5	6.5
C ₃ 's	2.7	5.7	6.7
C ₄ 's	0.8	1.7	2.0
C ₅ 's	0.8	1.7	2.0
Total gas	8.7	18.3	21.6%
BTX	3.6	7.6	9.0
C ₈ ⁺	22.8	47.9	56.6
Char residue	5.2	10.9	12.9
Totals	40.3	84.8	100.2

Table 4

Typical experimental run under reaction conditions

Run # Zn90

Final temperature = 523 °C

Heating rate = 237 °C/sec

Hydrogen pressure = 1000 psig

residence time = 3.95 seconds

catalyst/pitch ratio = 0.927 m/m

Product	mg C	% C of starting pitch	% C normalized
Methane	1.8	4.0	4.3
C ₂ 's	1.9	4.2	4.5
C ₃ 's	2.8	6.2	6.6
C ₄ 's	0.7	1.5	1.6
C ₅ 's	0.4	0.9	1.0
Total gas	7.6	16.8	17.9%
BTX	1.2	2.6	2.8
C ₈ +	30.4	67.1	71.5
Char residue	3.3	7.3	7.8
Totals	42.5	93.8	100.1

Table 5

Typical experimental run under reaction conditions

Run # Zn64

Final temperature = 593 °C

Heating rate = 274 °C/sec

Hydrogen pressure = 1000 psig

residence time = 3.95 seconds

catalyst/pitch ratio = 1.80 m/m

Product	mg C	% C of starting pitch	% C normalized
Methane	6.3	13.4	13.4
C ₁ 's	7.0	14.9	14.9
C ₂ 's	1.5	3.2	3.2
C ₃ 's	0.1	0.2	0.2
C ₄ 's	0.2	0.4	0.4
C ₅ 's			
Total gas	15.1	32.2	32.3%
BTX	5.4	11.5	11.5
C ₈ ⁺	19.2	41.0	41.1
Char residue	7.1	15.1	15.1
Totals	46.8	99.7	99.8

Table 6

Typical experimental run under reaction conditions

Run # Zn86

Final temperature = 582 °C

Heating rate = 238 °C/sec

Hydrogen pressure = 1000 psig

residence time = 3.95 seconds

catalyst/pitch ratio = 2.1 m/m

Product	mg C	% C of starting pitch	% C normalized
Methane	6.0	13.0	13.9
C ₂ 's	7.4	16.0	17.1
C ₃ 's	2.0	4.3	4.6
C ₄ 's	0.3	0.6	0.6
C ₅ 's	0.1	0.2	0.2
Total gas	15.8	34.2	36.6%
BTX	2.8	6.1	6.5
C ₈ +	16.5	35.7	38.2
Char residue	8.1	17.5	18.7
Totals	43.2	93.4	99.8

TABLE 17

Effect of Temperature on the Yield of Gases,
Liquids and Char Residue

Run Conditions:

Heating Rate = 237 C/sec
 Hydrogen Pressure = 1000 psig
 Residence Time = 3.95 sec
 Catalyst/Pitch = 0.93 m/m

Temperature ° C	product converted	Selectivity, wt % C			
		high boiling	gases	char residue	light boiling
330 (Zn 97)	5.0	6.0	0.0	94.0	0.0
530 (Zn 90)	92.5	71.0	17.5	7.5	3.0
730 (Zn 103)	87.0	40.0	38.0	13.5	8.5

* run # in brackets

TABLE 18

Effect of Heating Rate on the Yield of Gases,
Liquids and Char Residue

Run Conditions:

Final Temperature = 550^o C
 Hydrogen Pressure = 1000 psig
 Residence Time = 3.95 sec
 Catalyst/Pitch = 0.93 m/m

Heating Rate C/sec	product converted	Selectivity, wt % C			
		high boiling	gases	char residue	light boiling
120 (Zn 99)	85.5	63.5	8.0	14.5	13.5
240 (Zn 90)	92.5	71.0	17.5	7.0	2.5
300 (Zn 101)	88.0	43.5	33.5	12.0	6.5

* run # in brackets

TABLE 19

Effect of Residence Time on the Yield of Gases,
Liquids and Char Residue

Run Conditions:

Final Temperature = 550 °C
 Hydrogen Pressure = 1000 psig
 Heating Rate = 237 °C/sec
 Catalyst/Pitch = 0.93 m/m

Residence Time sec	product converted	Selectivity, wt % C			
		high boiling	gases	char residue	light boiling
2.50 (Zn 95)	85.5	54.5	26.5	14.0	4.5
4.00 (Zn 90)	92.5	71.5	17.5	8.0	3.0
10.85 (Zn 96)	88.5	60.0	22.5	12.0	5.5

* run # in brackets

TABLE 20

Effect of Pressure on the Yield of Gases,
Liquids and Char Residue

Run Conditions:

Final Temperature = 550^o C

Heating Rate = 237^o C/sec

Residence Time = 3.95 sec

Catalyst/Pitch = 0.93 m/m

Pressure psig	product converted	Selectivity, wt % C			
		high boiling	gases	char residue	light boiling
250 (Zn 93)	92.0	78.5	7.5	9.0	4.0
500 (Zn 107)	91.5	72.5	16.0	8.5	3.0
1000 (Zn 90)	92.0	71.5	18.0	7.5	2.5
1400 (Zn 94)	87.5	66.0	10.5	13.0	10.5

* run # in brackets

TABLE 21

Effect of Temperature on % Yield
of Various Gaseous Product Distribution

Temperature °C	Selectivity, wt % C				
	methane	ethane	propane	ethene	propene
333 (Zn 97)	0.0	0.0	0.0	0.0	0.0
525 (Zn 90)	4.0	2.4	3.6	2.0	2.7
701 (Zn 103)	30.0	6.8	0.6	1.0	0.6

* run # in brackets

TABLE 22

Effect of Heating Rate on % Yield
of Various Gaseous Product Distribution

Heating Rate C/sec	Selectivity, wt % C				
	methane	ethane	propane	ethene	propene
119 (Zn 99)	2.5	2.3	3.2	1.7	3.0
237 (Zn 90)	4.1	2.7	3.7	1.9	2.5
309 (Zn 101)	12.7	12.0	4.4	1.6	1.1

* run # in brackets

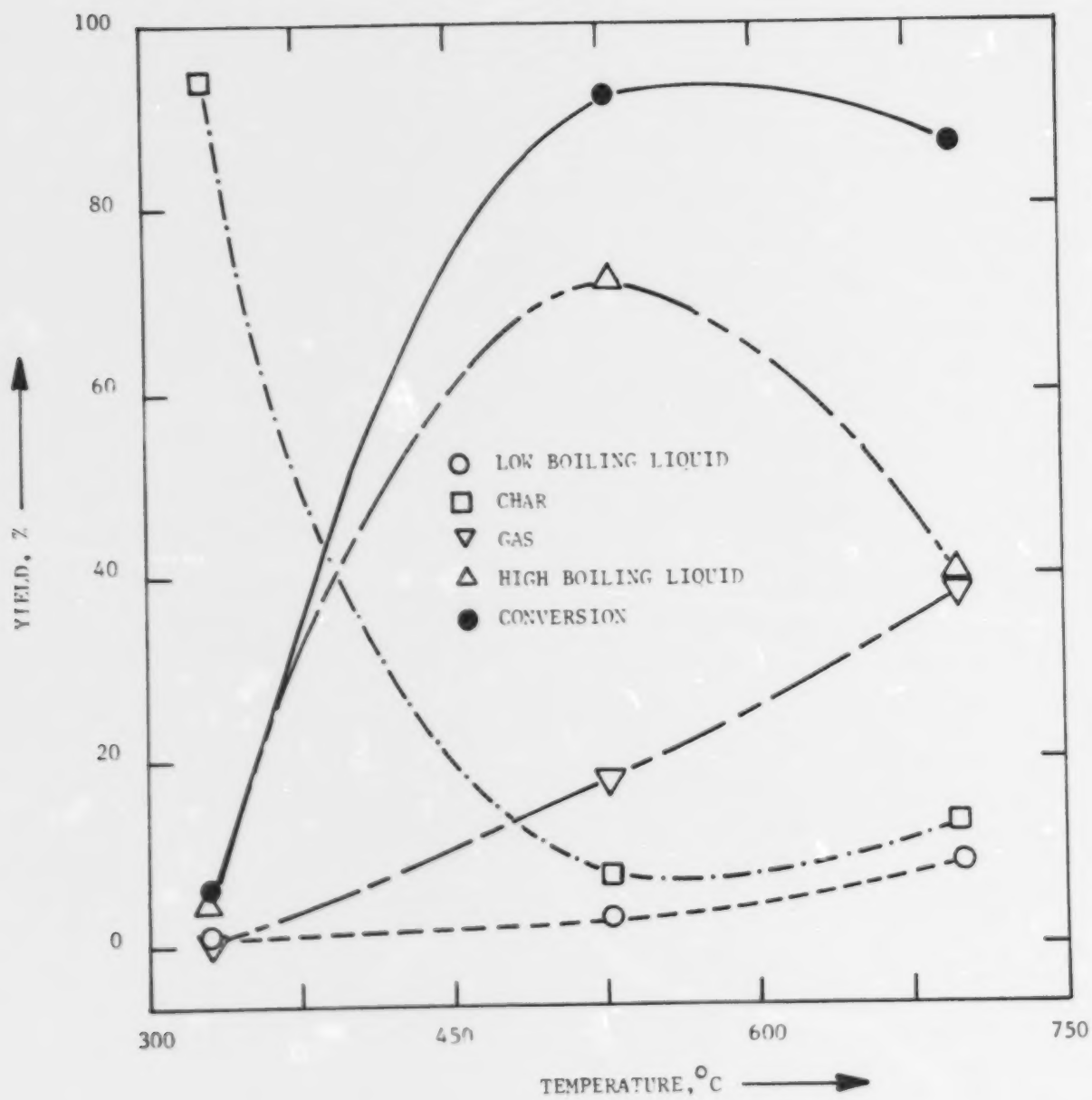


FIGURE: 33 A plot of yield versus reactor temperature, conditions:
 Heating rate 237°C/sec., H_2 pressure 1,000 psi
 Residence time 3.95 sec.
 Catalyst/pitch ratio = 0.93

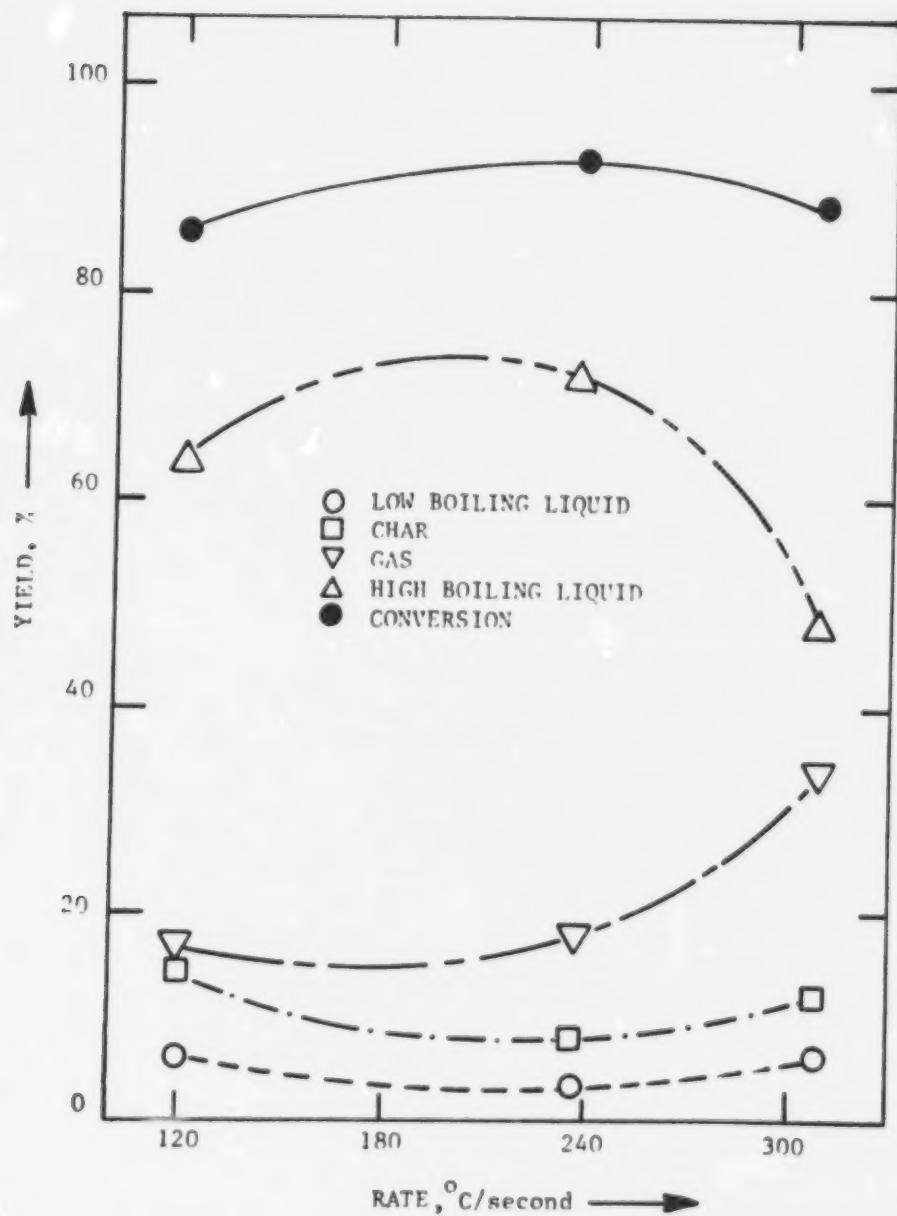


FIGURE: 34 A plot of yield versus heating rate.
conditions: Final temperature 550°C, H₂ pressure
1,000 psi, Residence time 3.95 sec., catalyst/pitch
ratio = 0.93

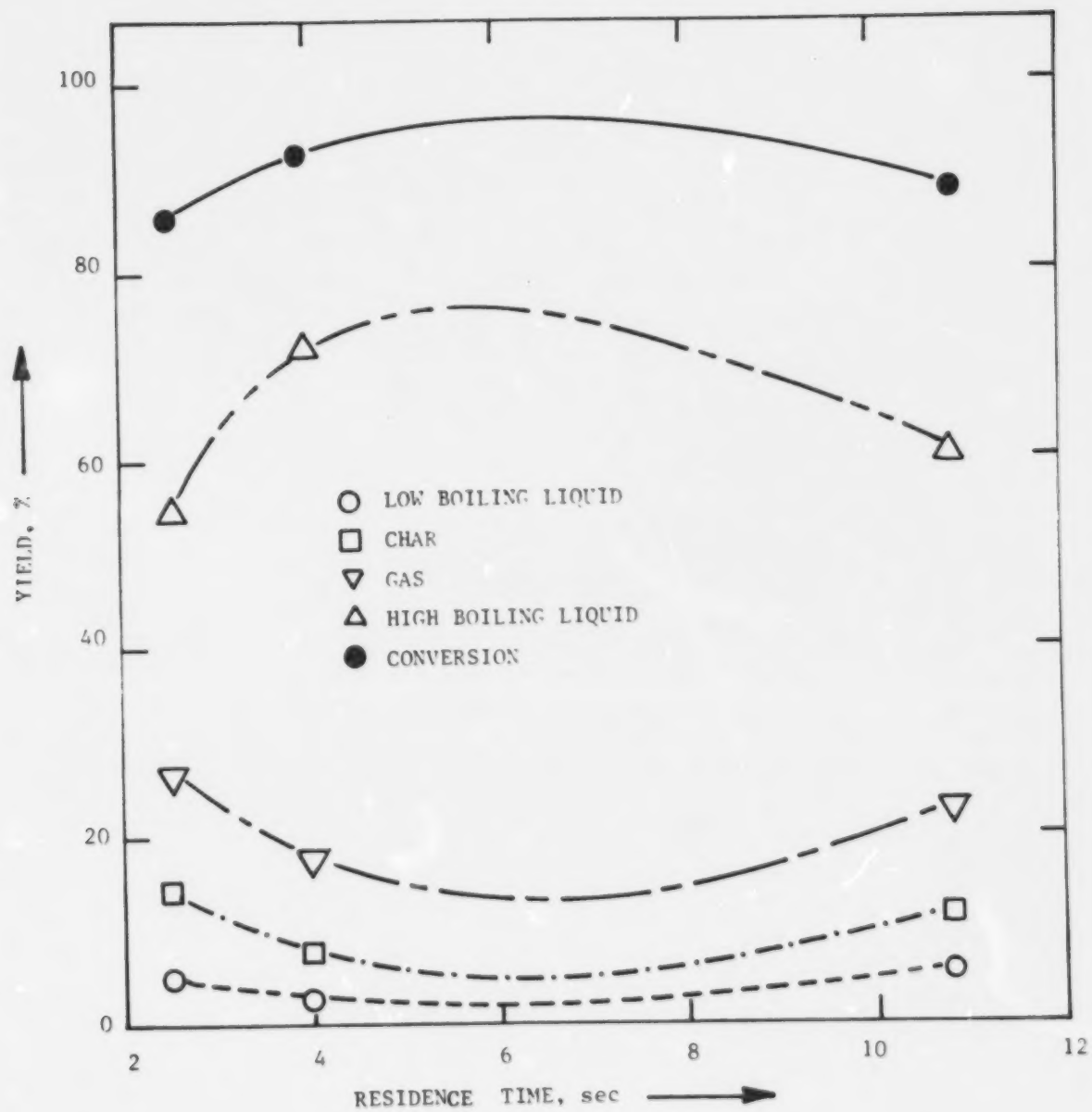


FIGURE: 35 A plot of yield versus residence time. Conditions: Heating rate 237°C/sec, Final temperature 550°C, H₂ pressure 1,000 psi., catalyst/pitch ratio = 0.93.

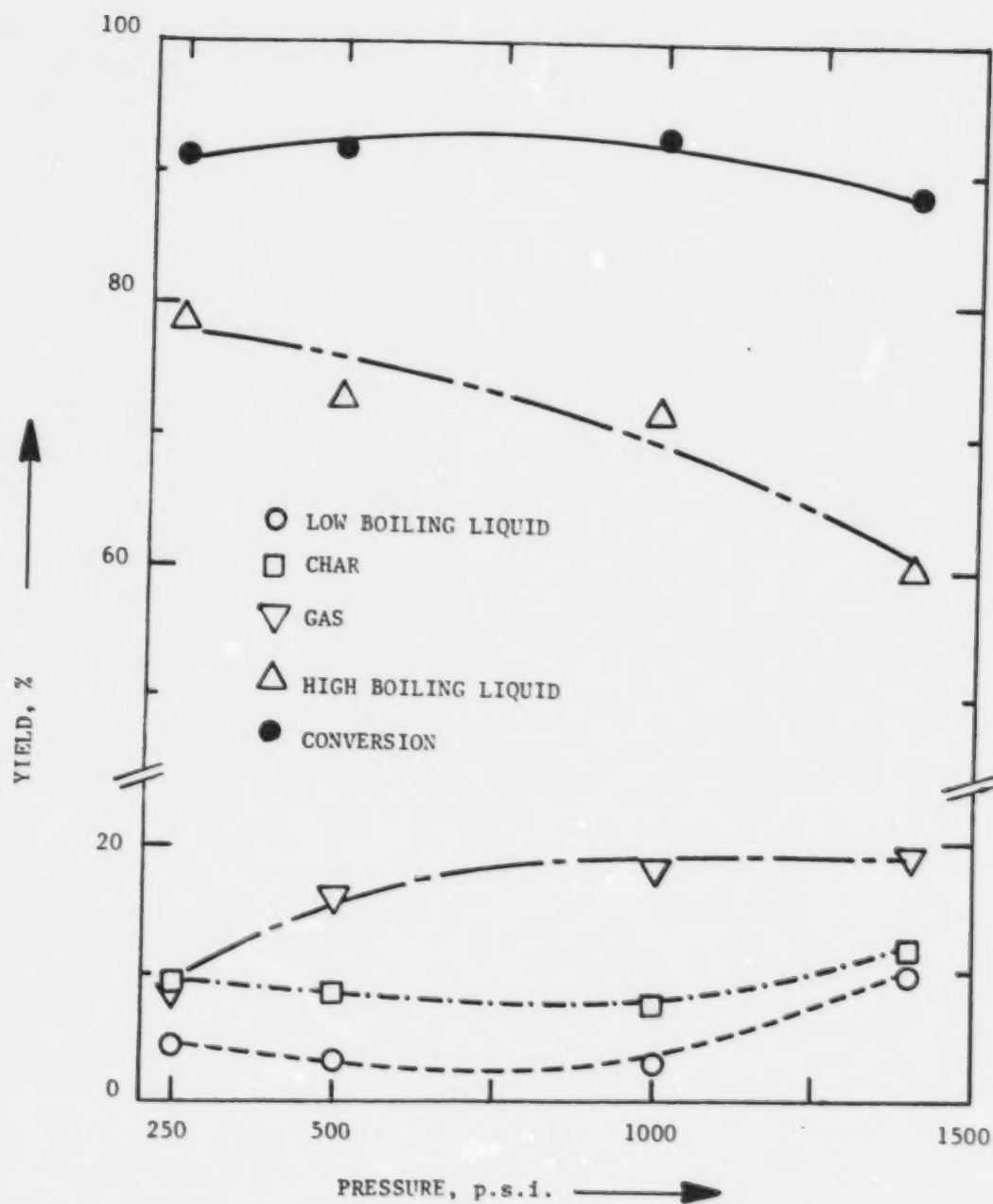


FIGURE: 36 A plot of yield versus reactor pressure. Conditions: Heating rate $237^{\circ}\text{C}/\text{sec}$, Final temperature 550°C , Residence time 3.95 sec., Catalyst/pitch ratio = 0.93.

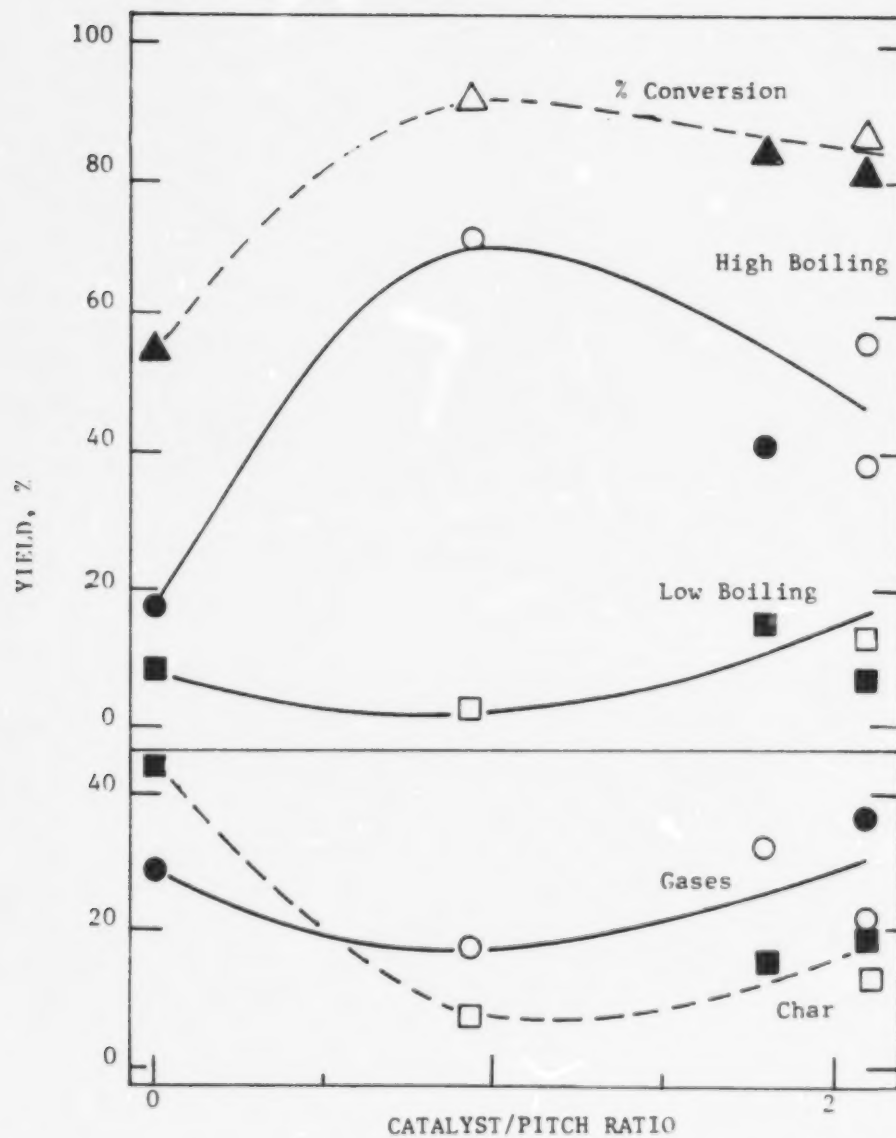


FIGURE: 37 A plot of yield versus Catalyst/pitch ratio. Conditions: Heating rate = 237°C/S , Hydrogen Pressure = 1000 psi, final temperature = 550°C , Residence Time = 3.95 sec. Open data points represent final temperature of $510 - 520^{\circ}\text{C}$. Solid data points represent final temperatures of $580 - 590^{\circ}\text{C}$.

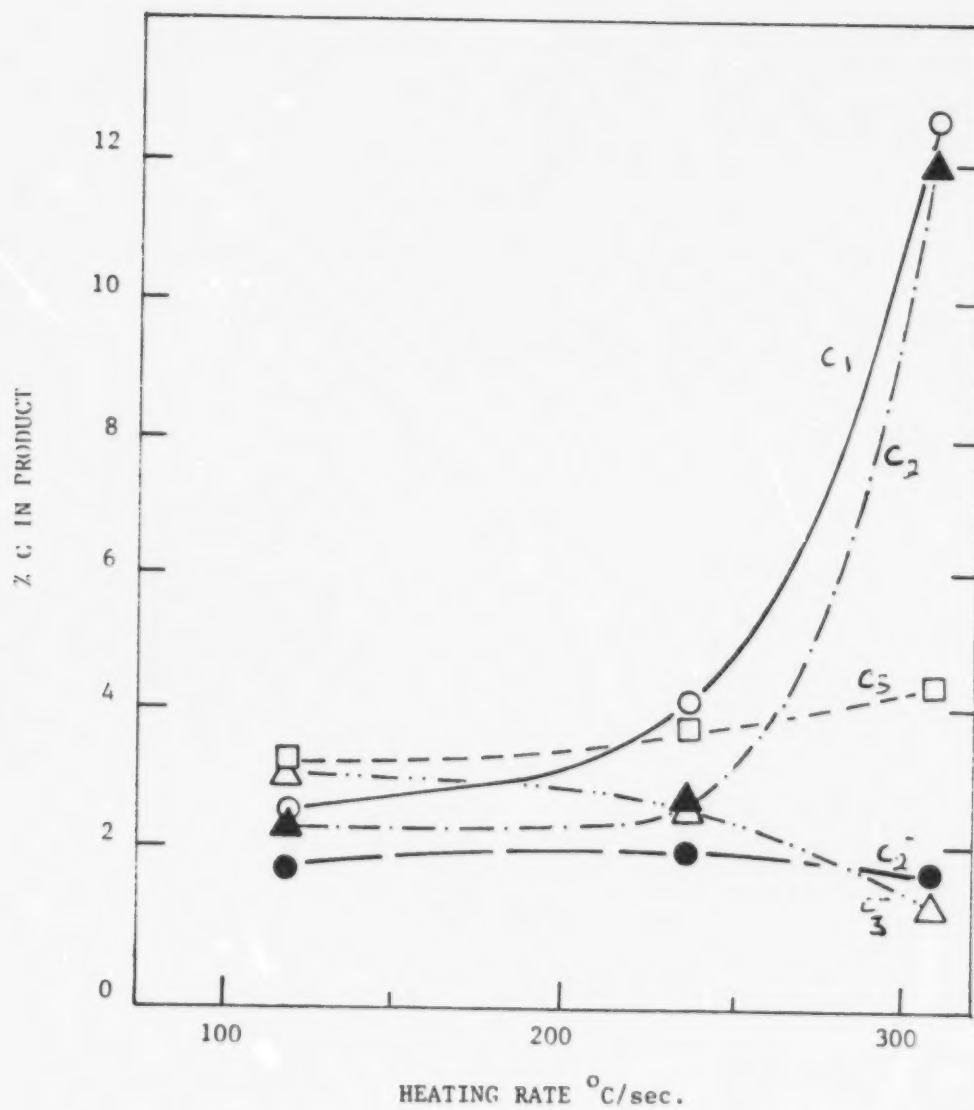


FIGURE: 38 A plot of gaseous product distribution versus heating rate, conditions. Hydrogen pressure = 1000 psi, Final Temperature = 550°C, Catalyst to Pitch Ratio = 0.93.

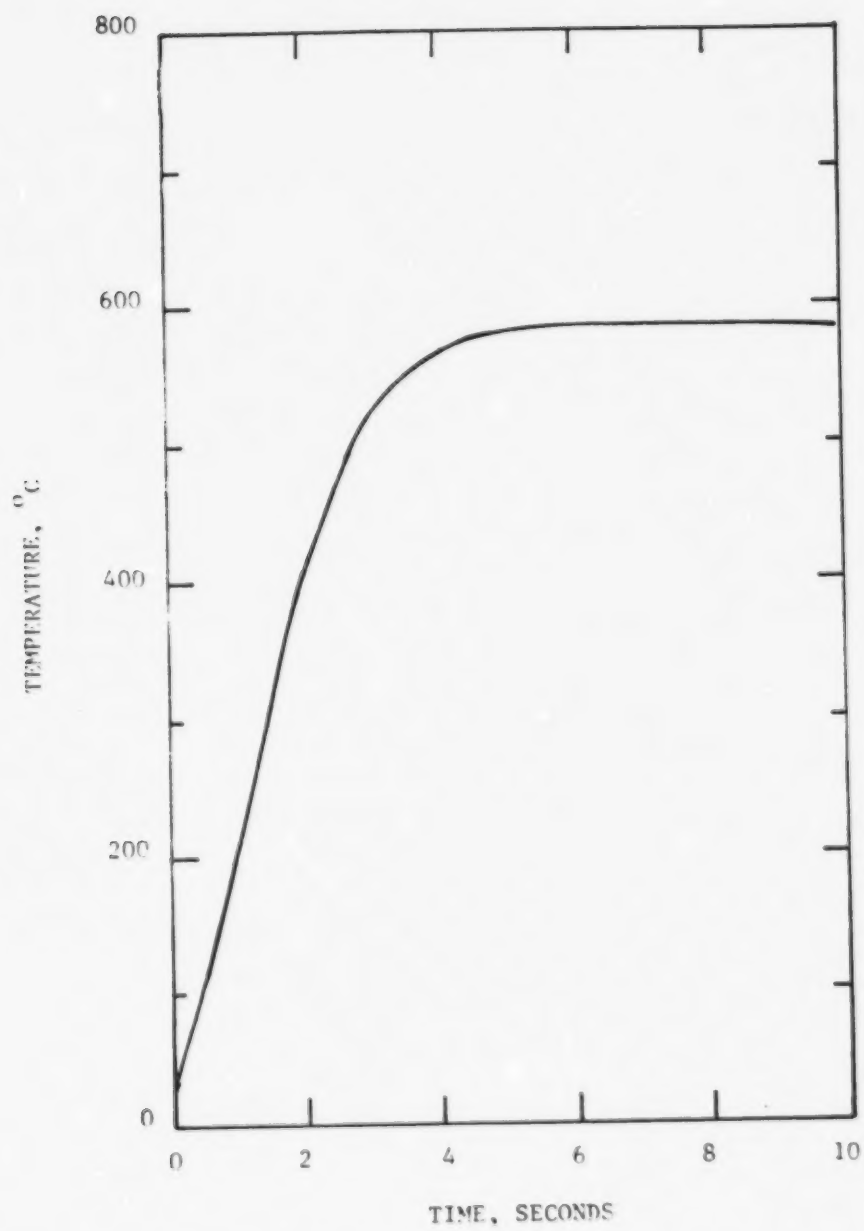


FIGURE: 39 Reactor Temperature versus time curve
Run No. Pitch Zn 86.

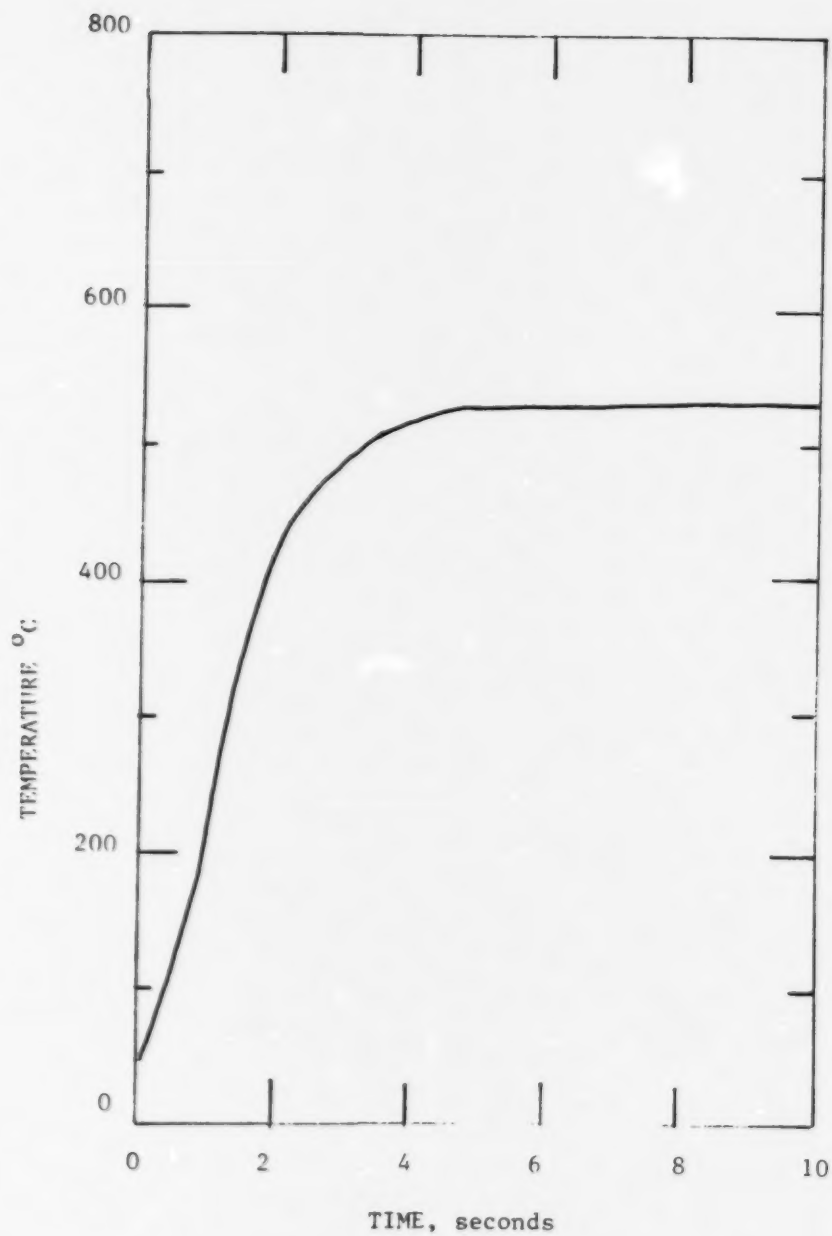


FIGURE: 40 Reactor temperature versus time curve. Run No. Pitch Zn 90.

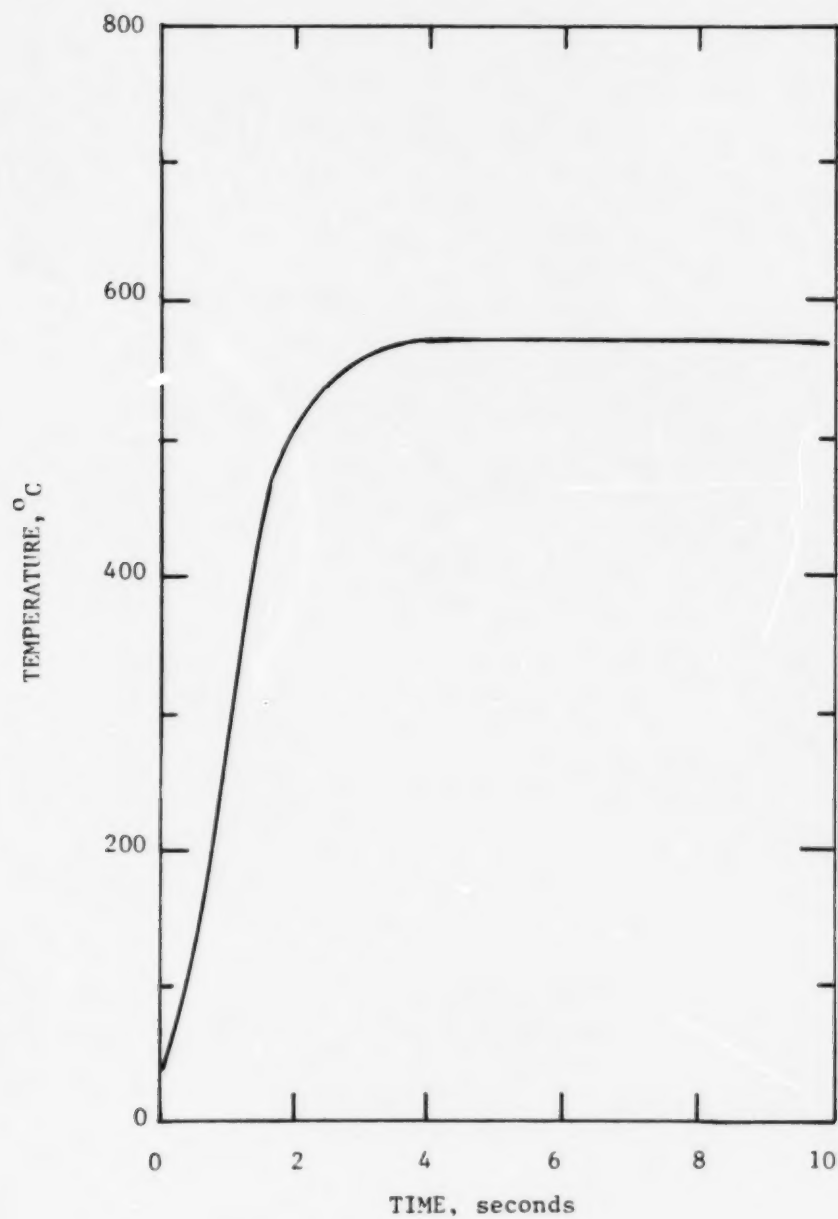


FIGURE: 41 Reactor temperature versus time curve. Run No. Pitch Zn 91.

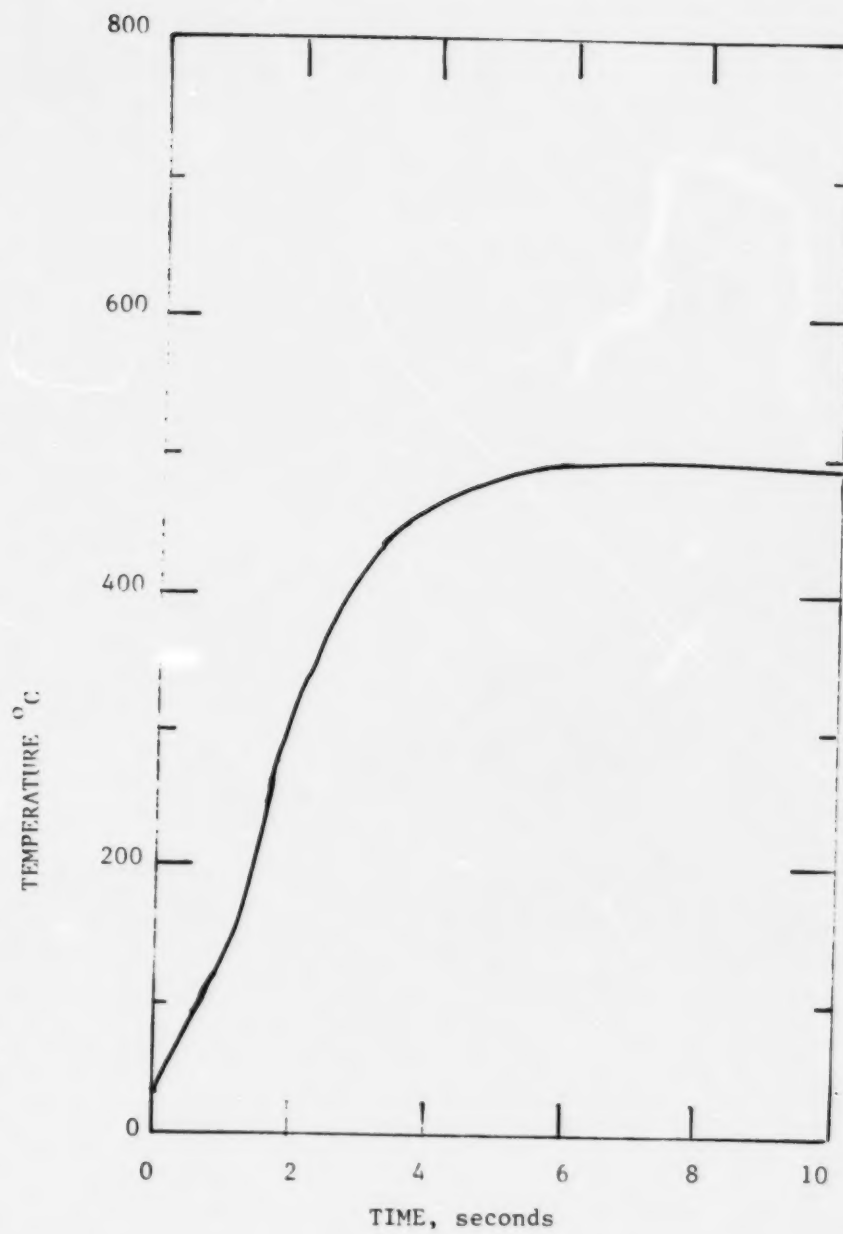


FIGURE: 42 Reactor temperature versus time curve. Run No. Pitch Zn 93.

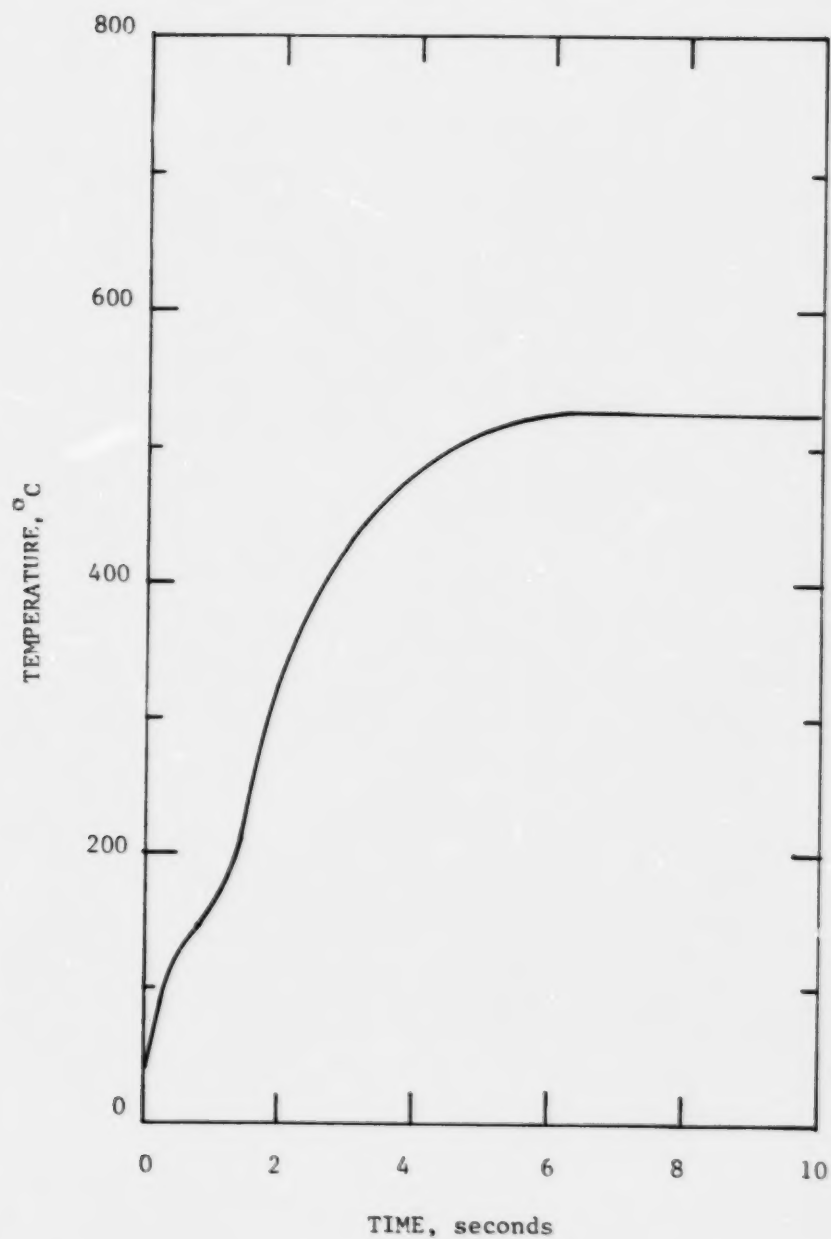


FIGURE:43 Reactor temperature versus time curve. Run No. Pitch Zn 94.

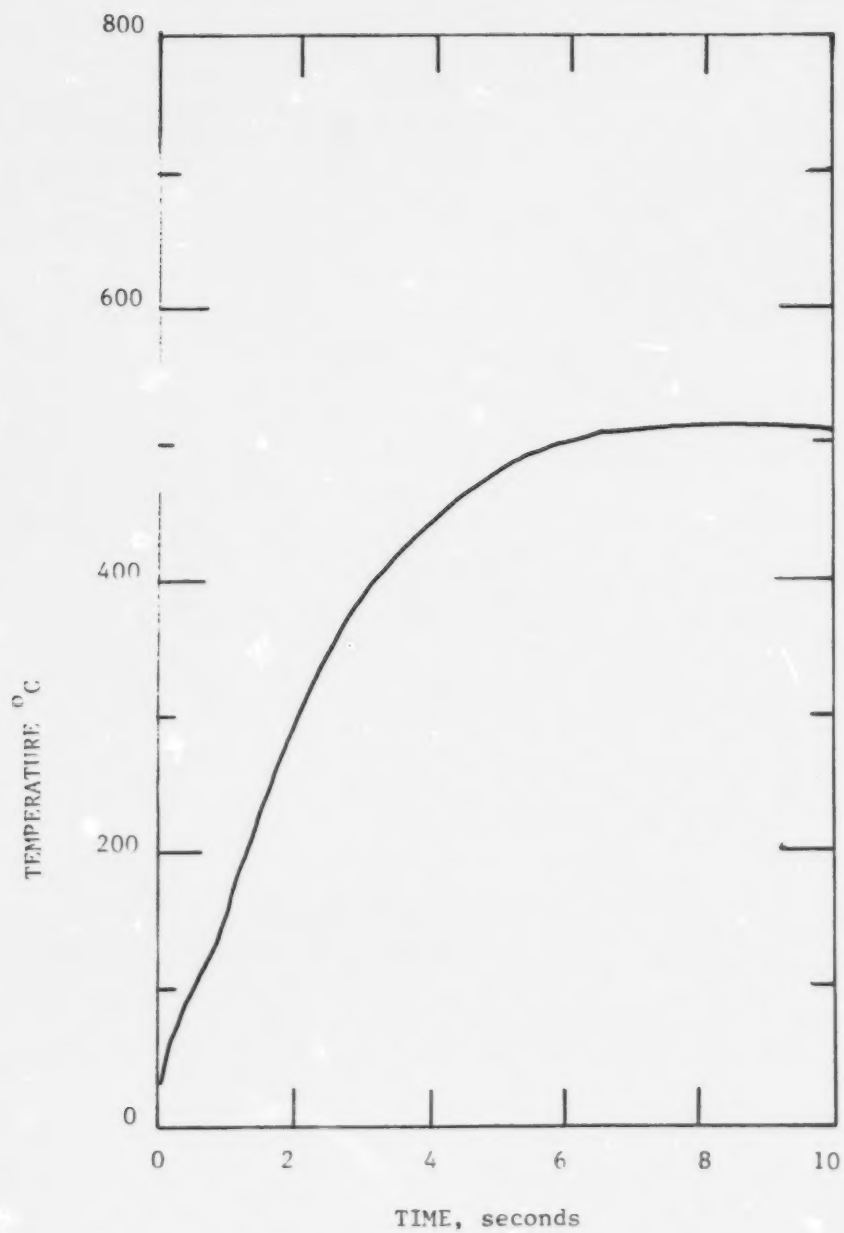


FIGURE: 44 Reactor temperature versus time curve. Run No. Pitch Zn 95.

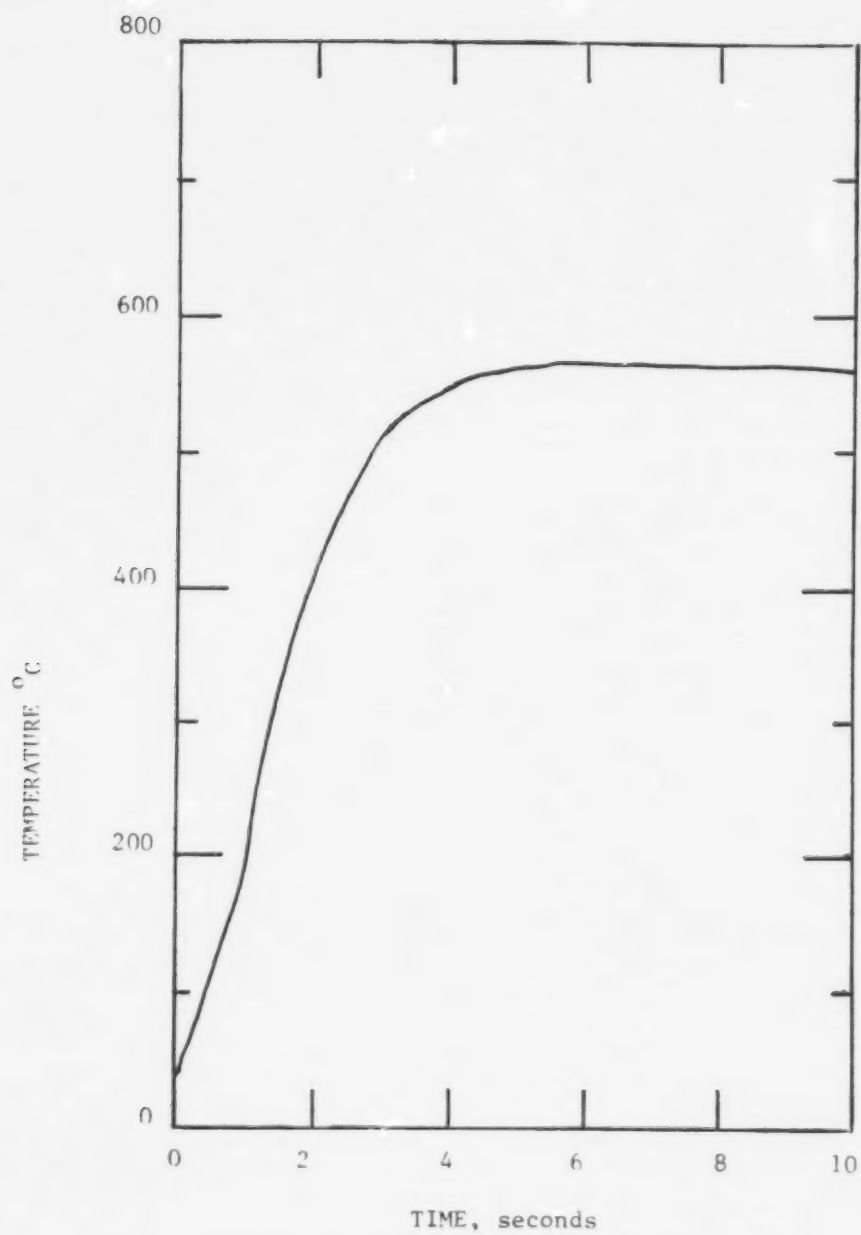


FIGURE: 45 Reactor temperature versus time curve. Run No. Pitch Zn 96.

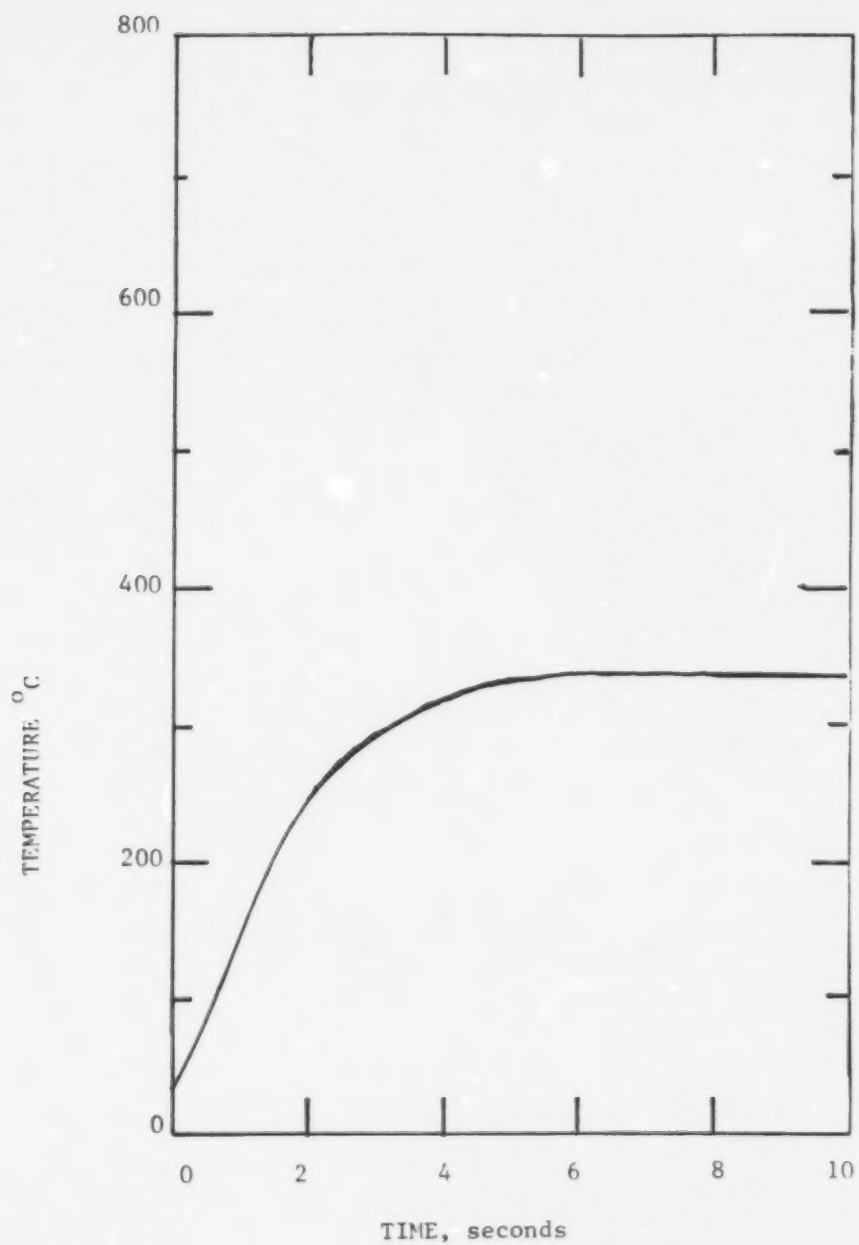


FIGURE:46 Reactor temperature versus time curve. Run No. Pitch Zn 97

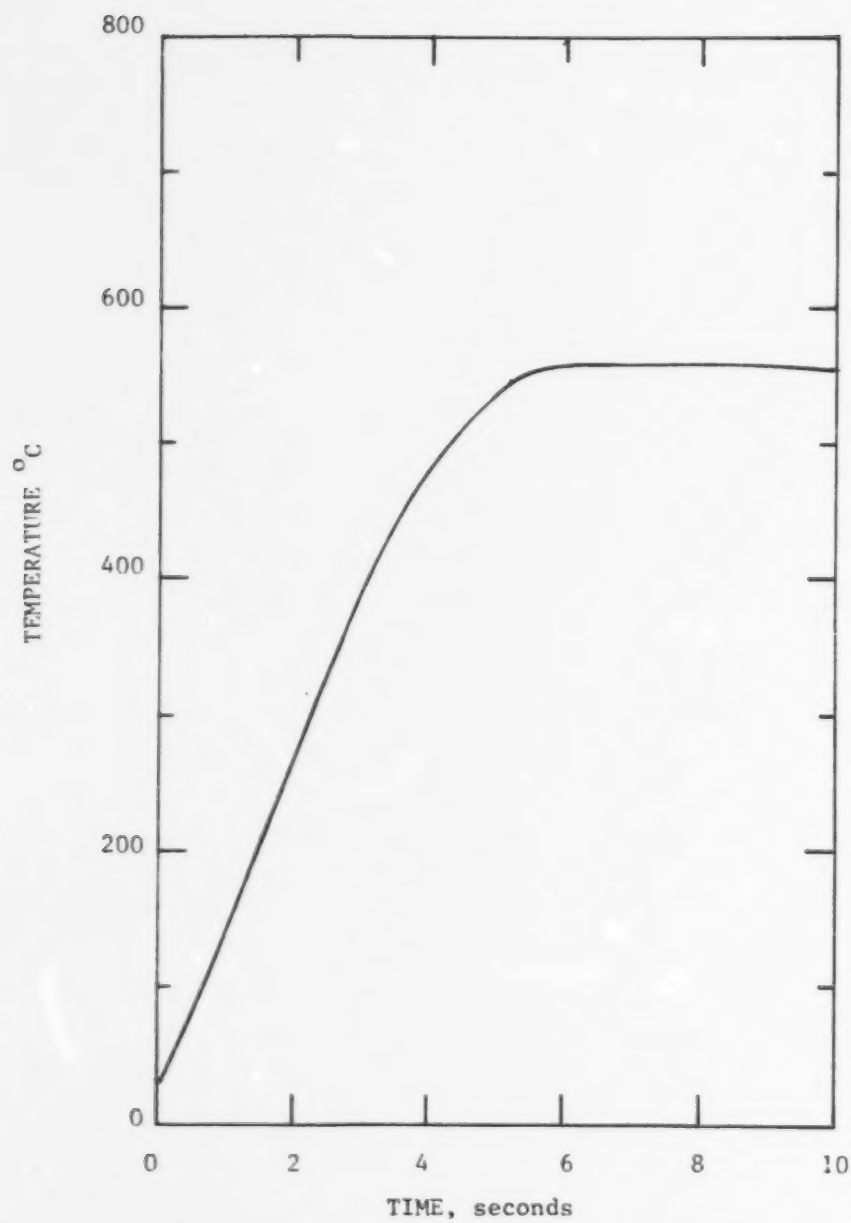


FIGURE: 47 Reactor temperature versus time curve. Run No. Pitch Zn 99.

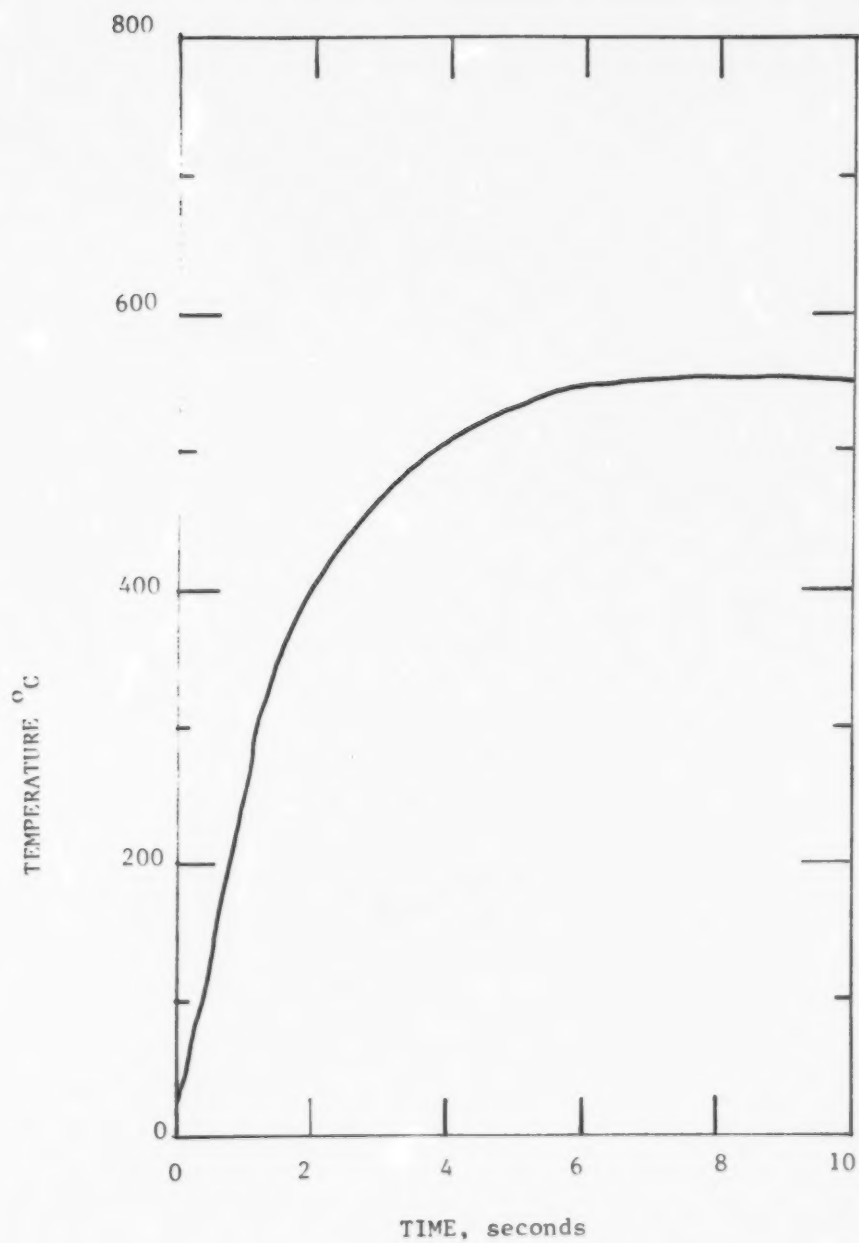


FIGURE:48 Reactor temperature versus time curve. Run No. Pitch Zn 101

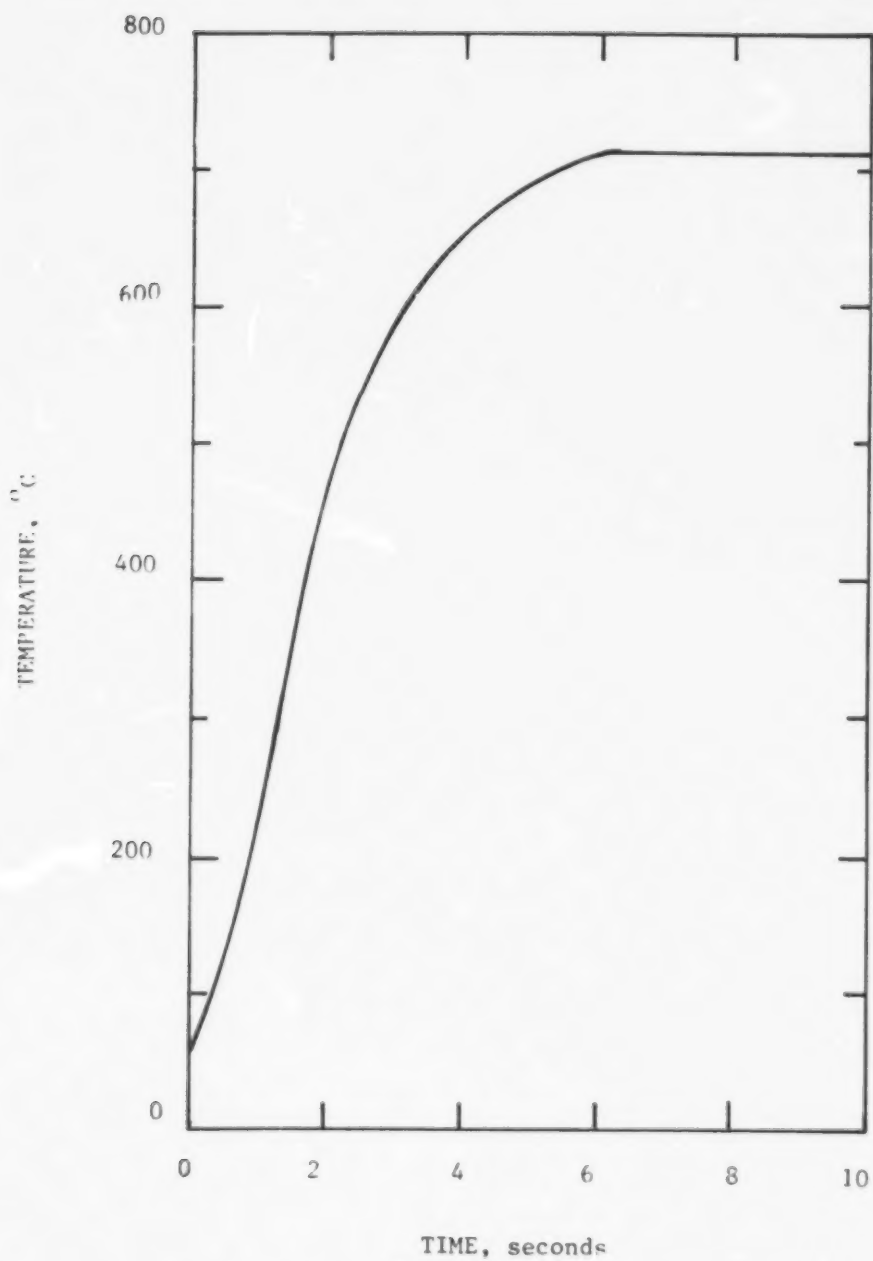


FIGURE: 49 Reactor temperature versus time curve. Run No. Pit Zn 103.

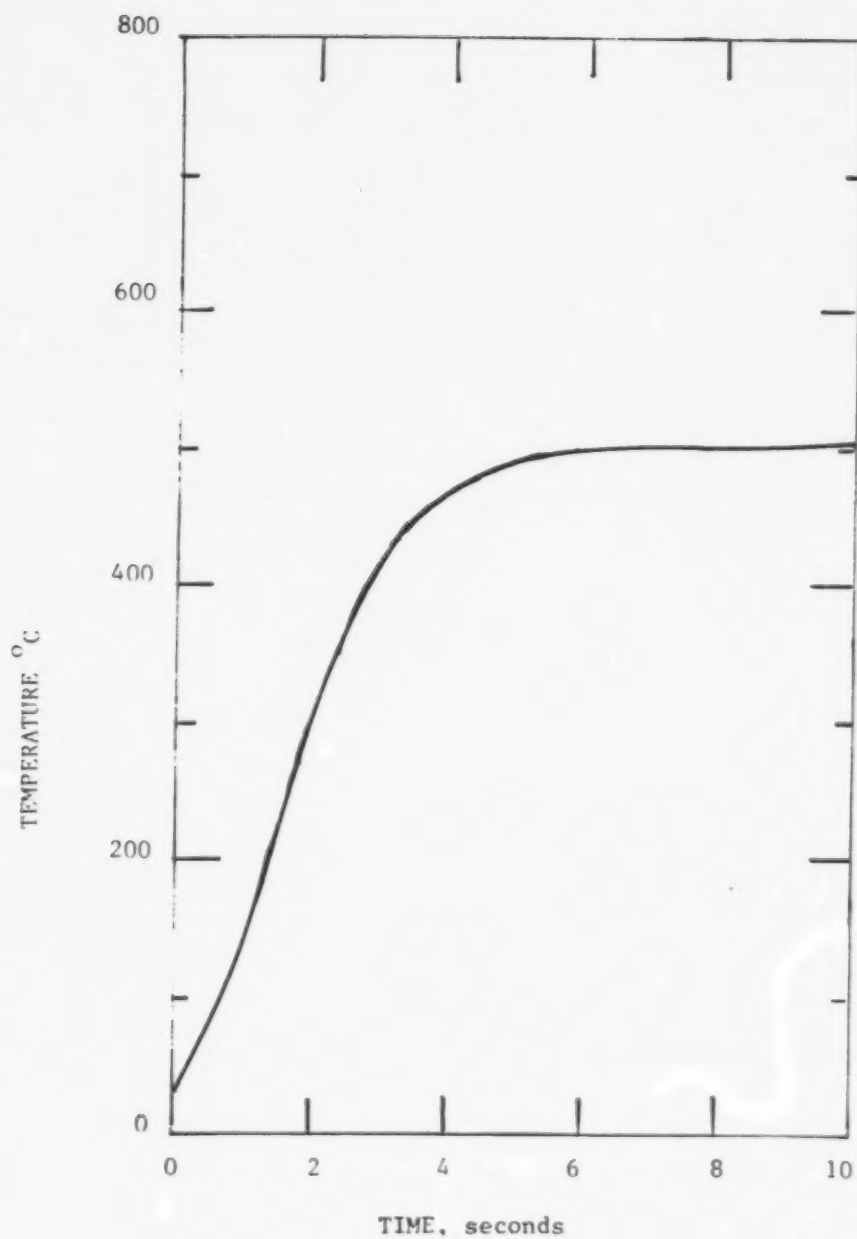


FIGURE: 50 Reactor Temperature versus time curve. Run No. Pitch Zn 107.

FIGURE: 51 Heavy Liquid
Cumulative % boiling off vs. Temperature
Catalyst ZnCl_2
Run # Zn90

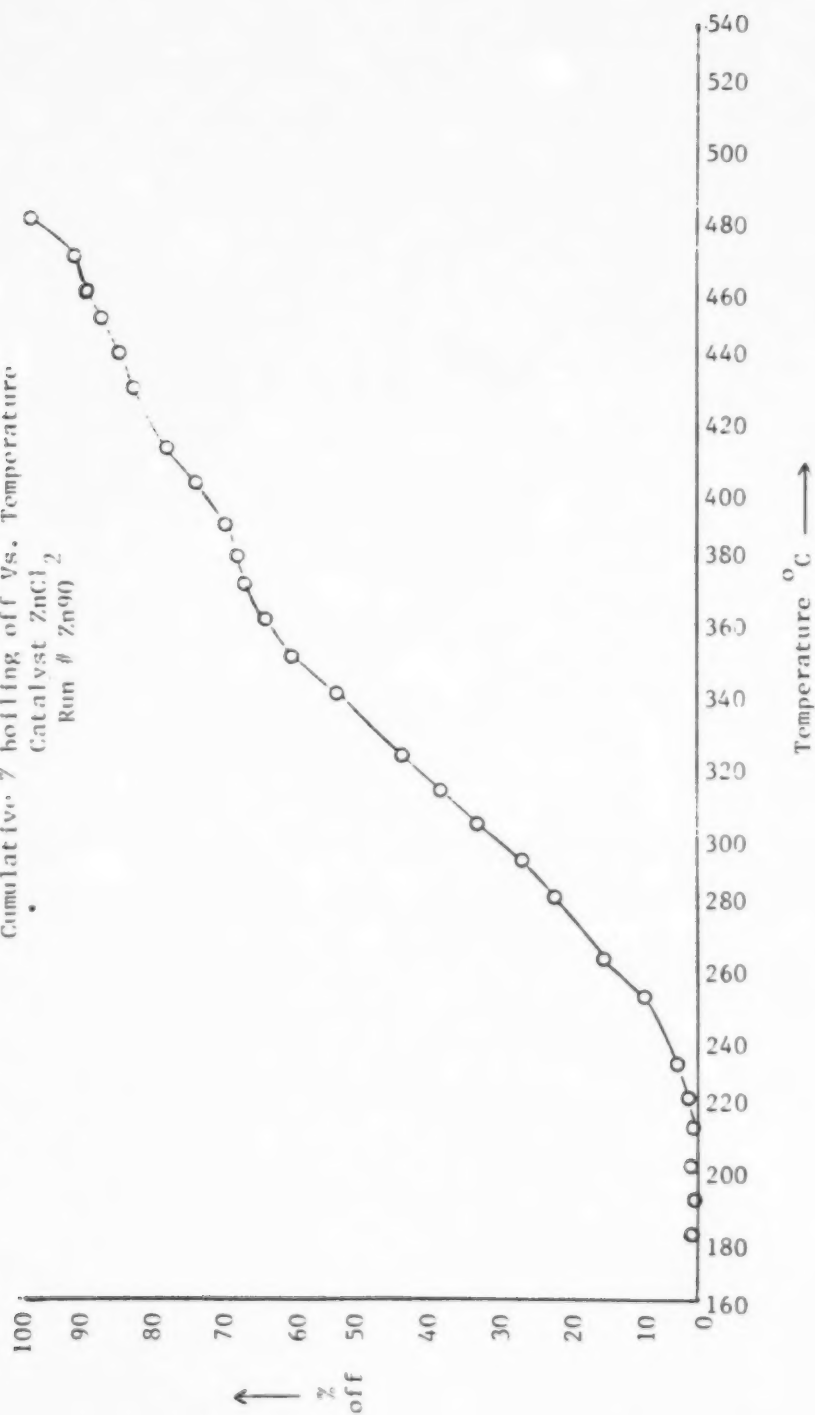


FIGURE: 52 Histogram of % Boiling Distribution
in the FHP of Pitch with ZnCl_2
Run # Zn90

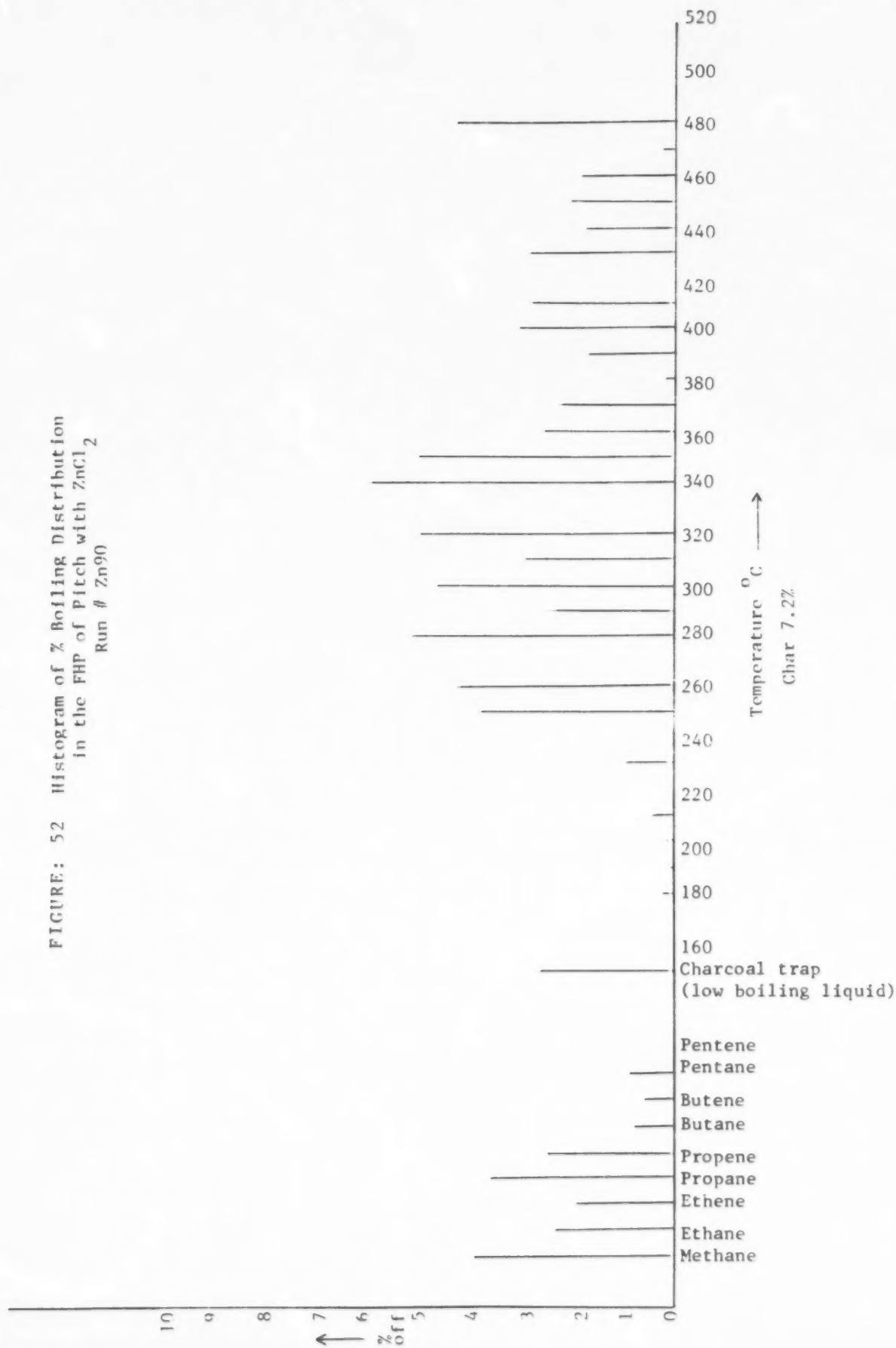


FIGURE:53 Heavy Liquid
Typical Cumulative % boiling off Vs. Temperature
Catalyst ZnCl_2
Run # pitch 7n93

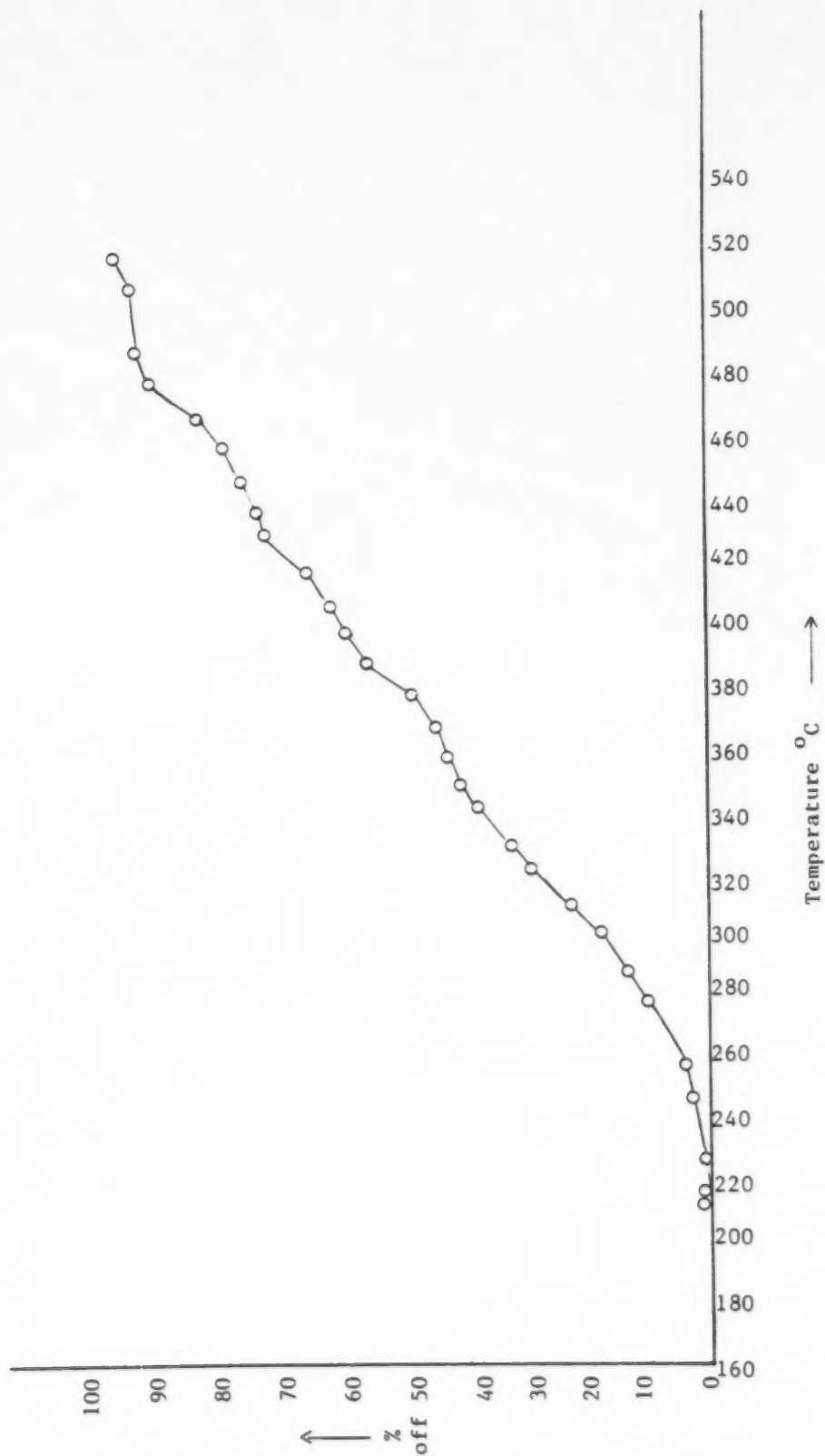


FIGURE: 54 Histogram of % Boiling Distribution
of Pitch Catalyzed by ZnCl_2
Run # pitch Zn93

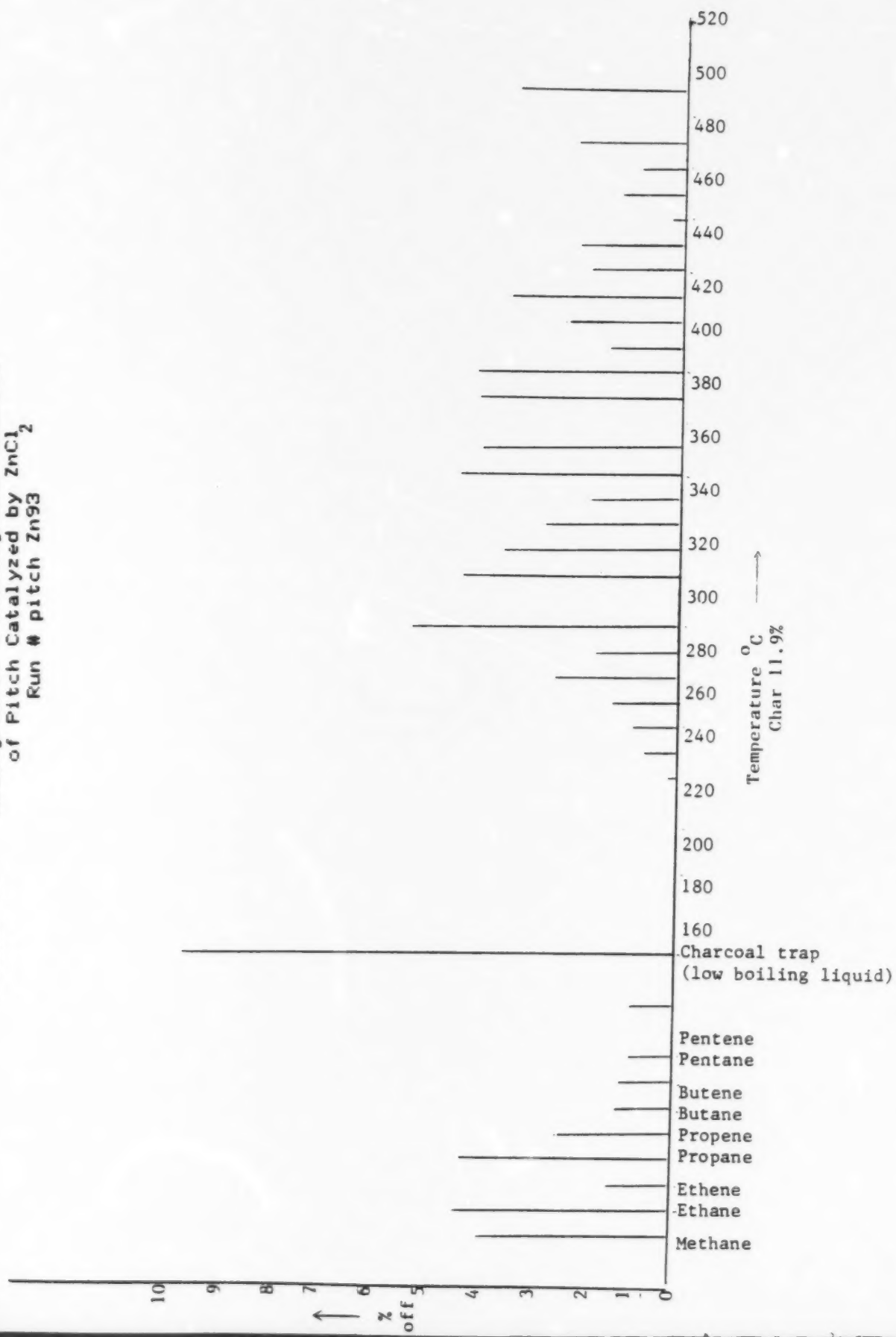


FIGURE: 55 Heavy Liquid
Typical Cumulative % boiling off Vs. Temperature
Catalyst ZnCl_2
Run # pitch Zn96

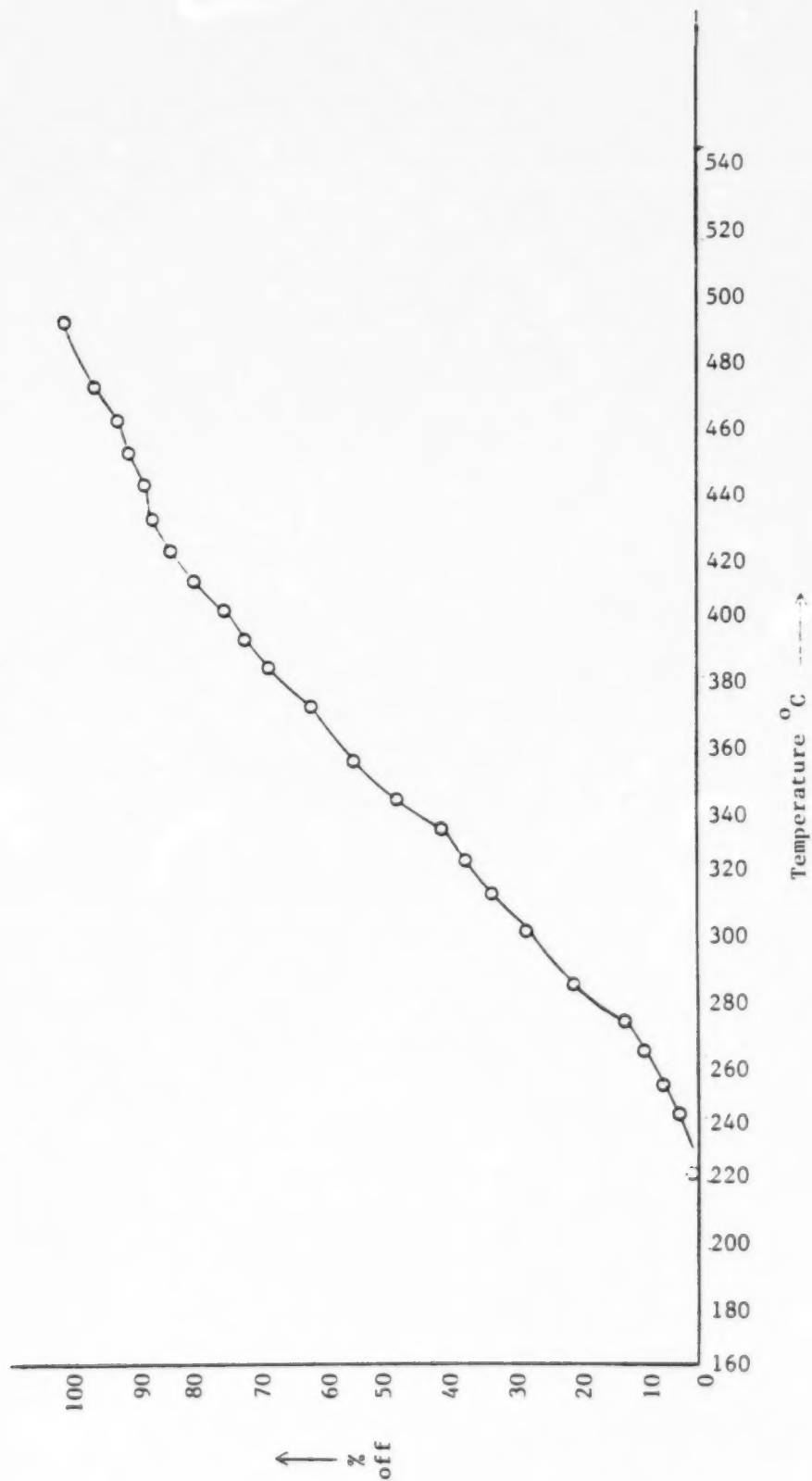


FIGURE: 56 Histogram of % Boiling Distribution
of Pitch Catalyzed by ZnCl_2
Run # pitch Zn96

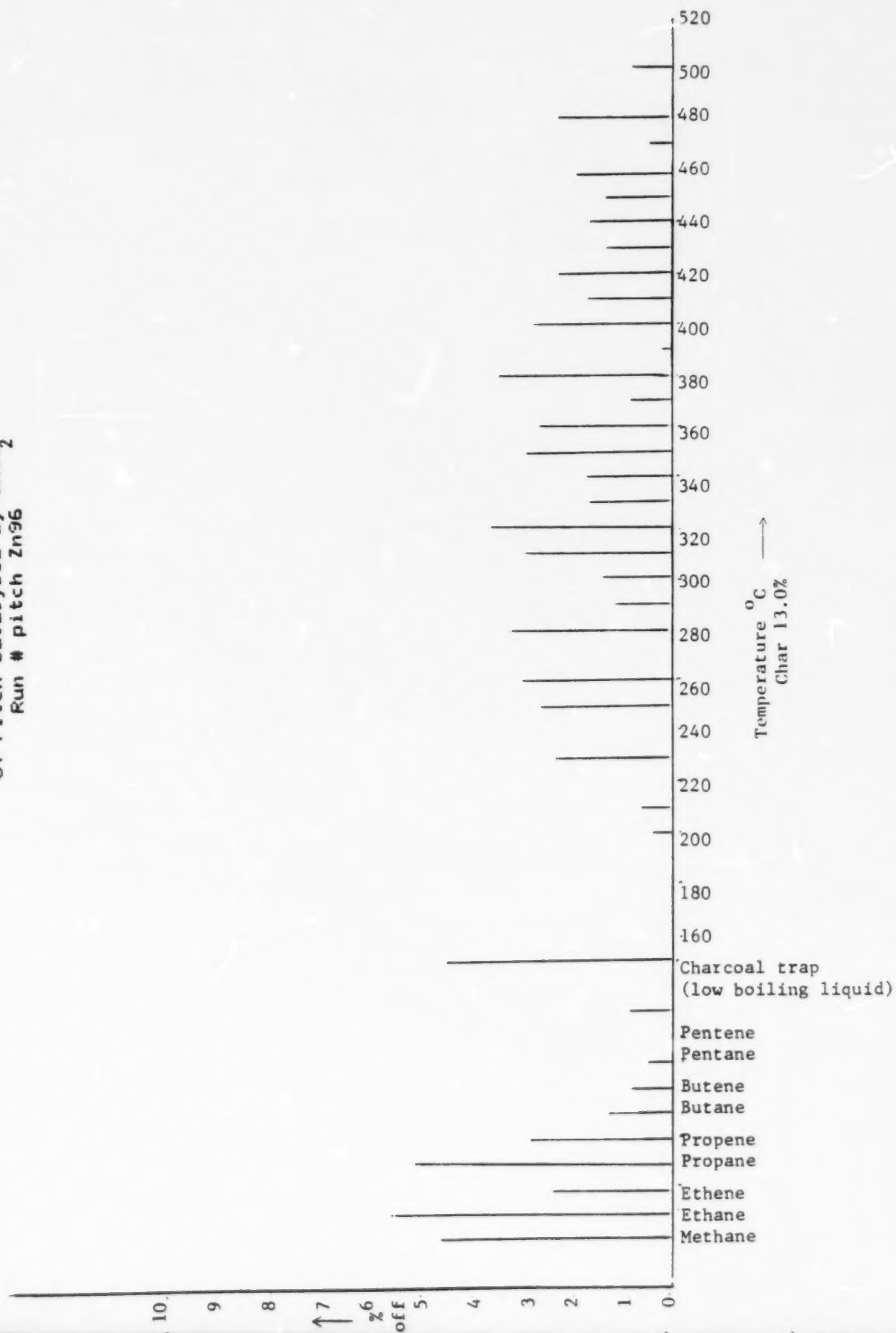


FIGURE: 57 Heavy Liquid
Typical Cumulative % boiling off Vs. Temperature
Catalyst ZnCl_2
Run # pitch Zn99

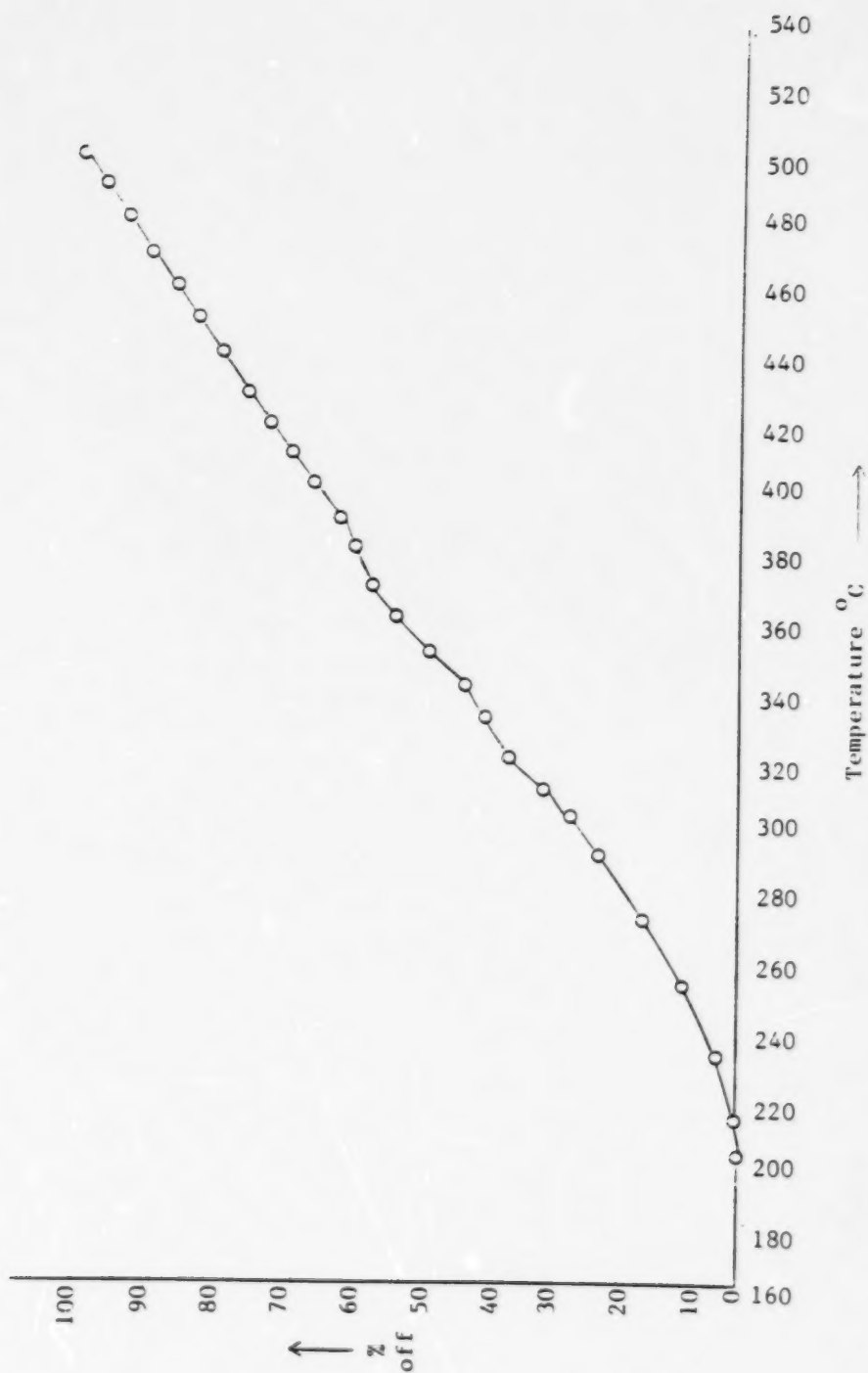


FIGURE: 58 Histogram of % Boiling Distribution
of Pitch Catalyzed by ZnCl_2
Run # pitch Zn99

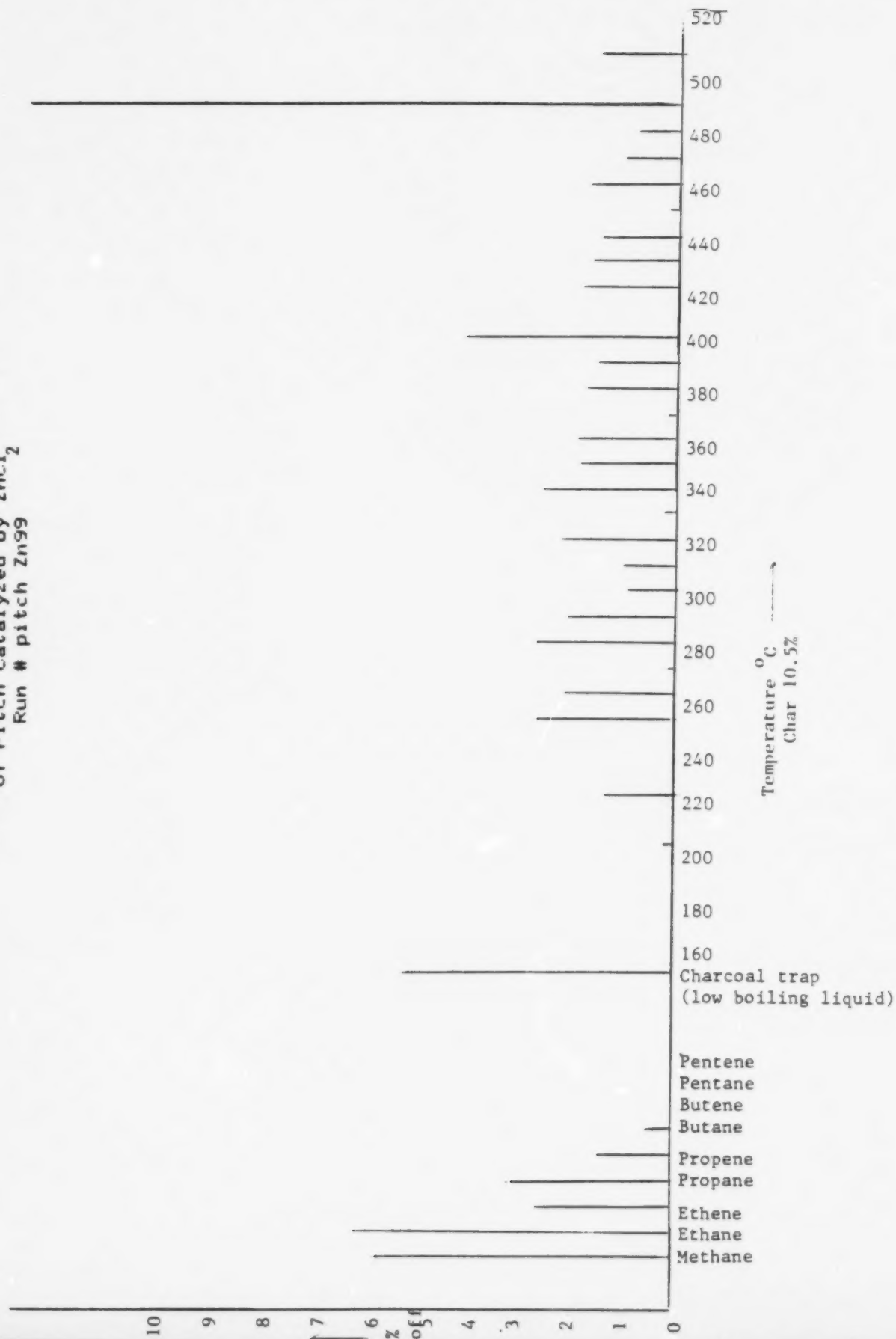


FIGURE: 59 Heavy Liquid
Cumulative % boiling off Vs. Temperature
Catalyst ZnCl_2
Run # Zn101

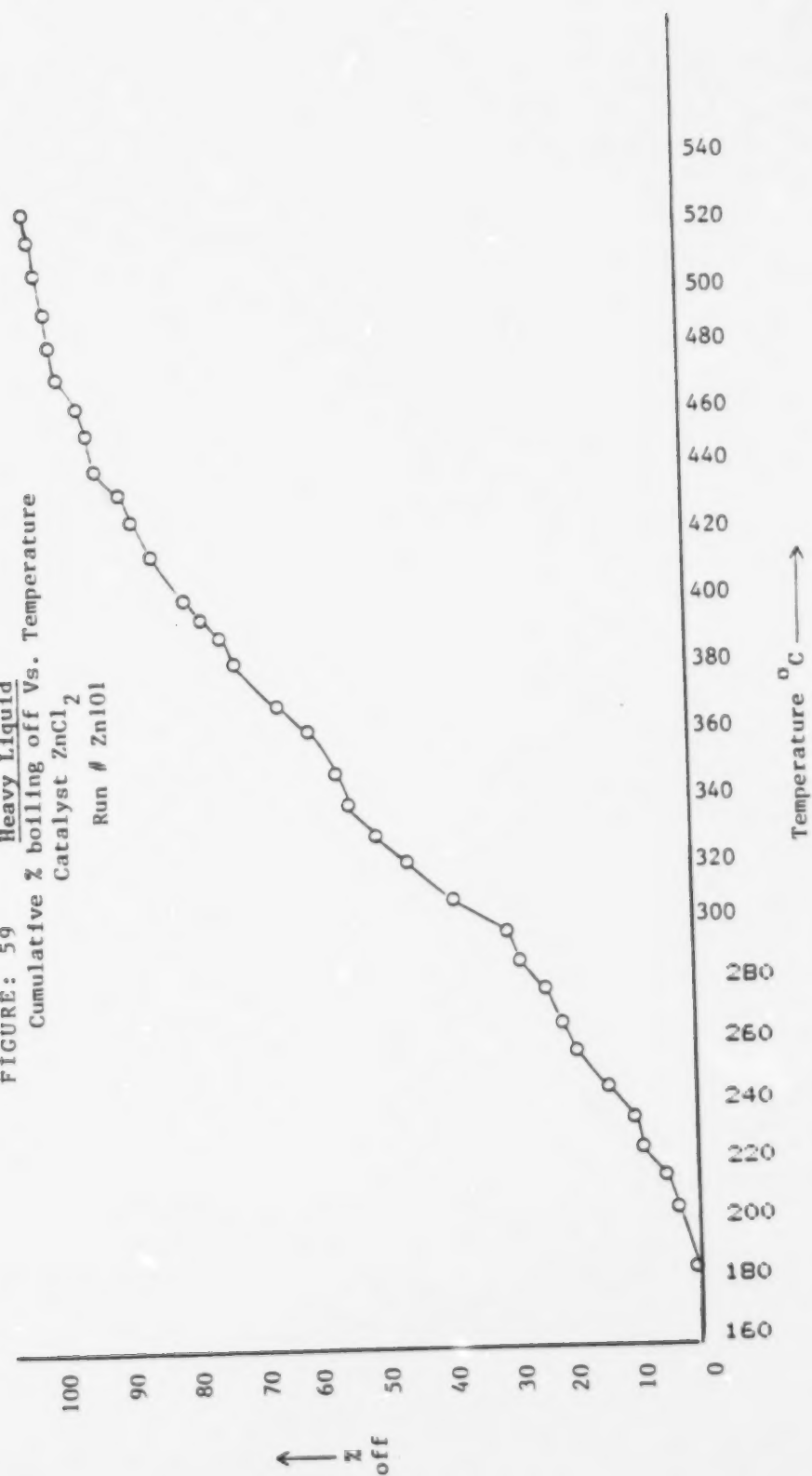


FIGURE: 60 Histogram of % Boiling Distribution
in the FHP of Pitch with ZnCl_2

Run # Zn101

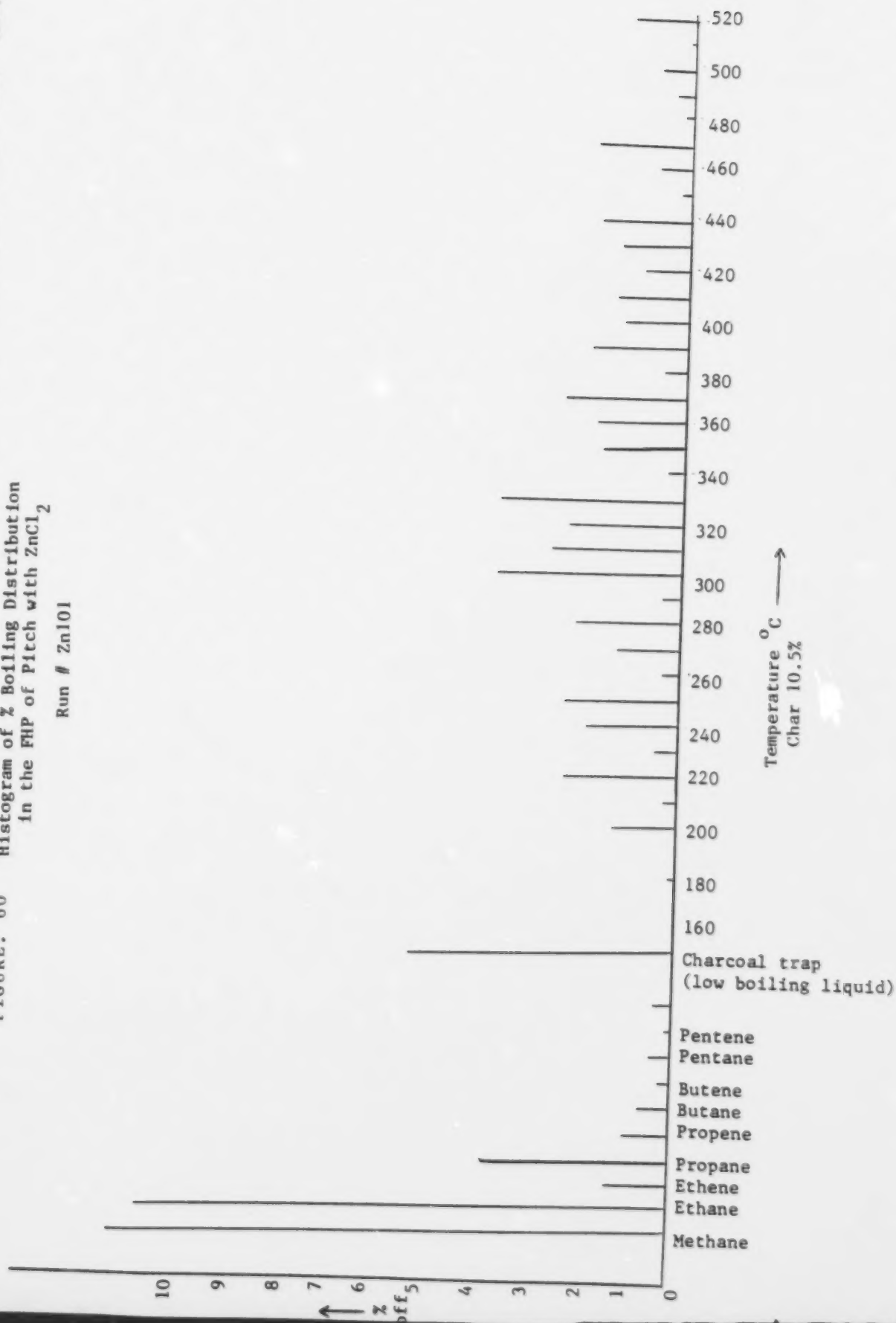
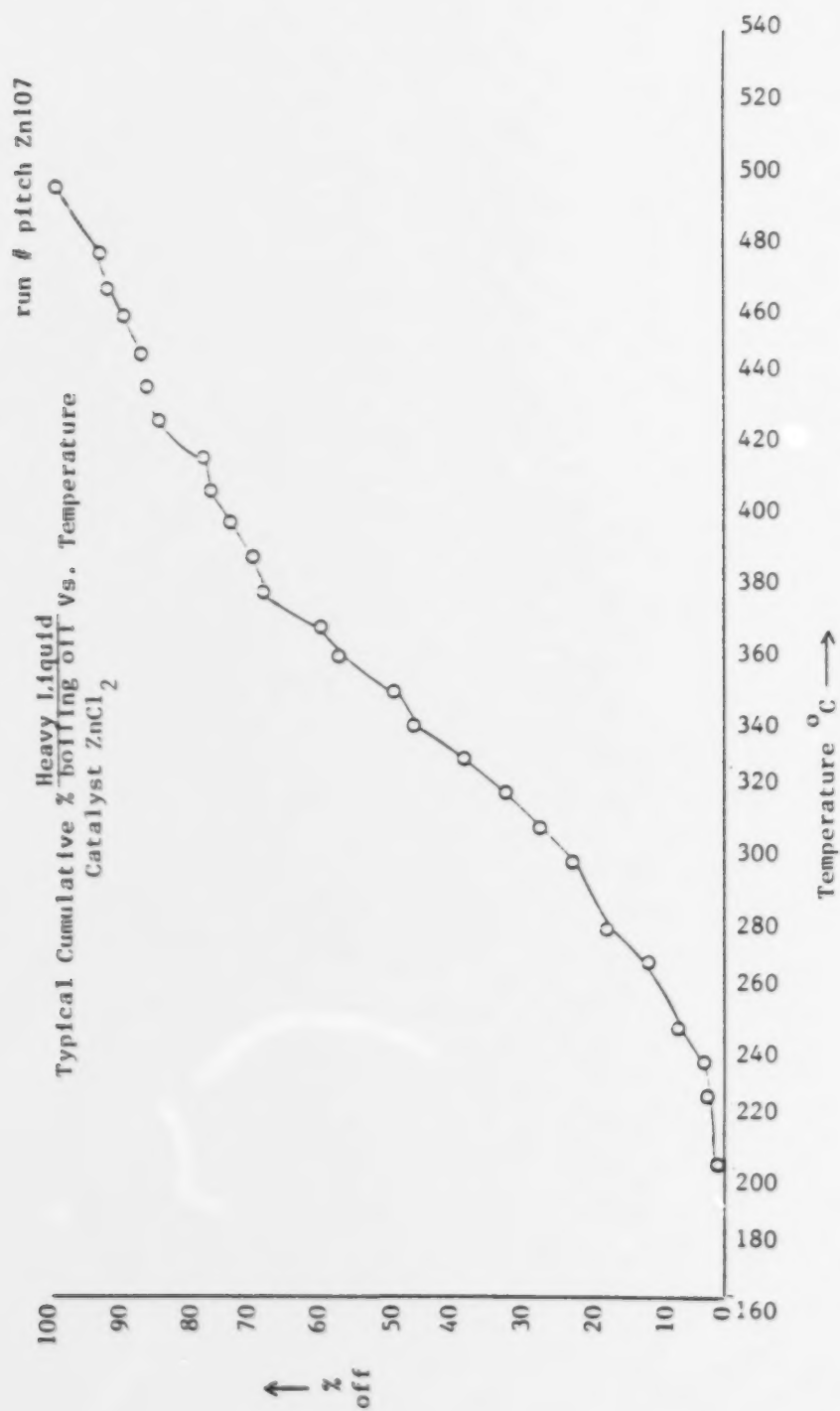


FIGURE: 61



run # pitch Zn107

FIGURE: 62

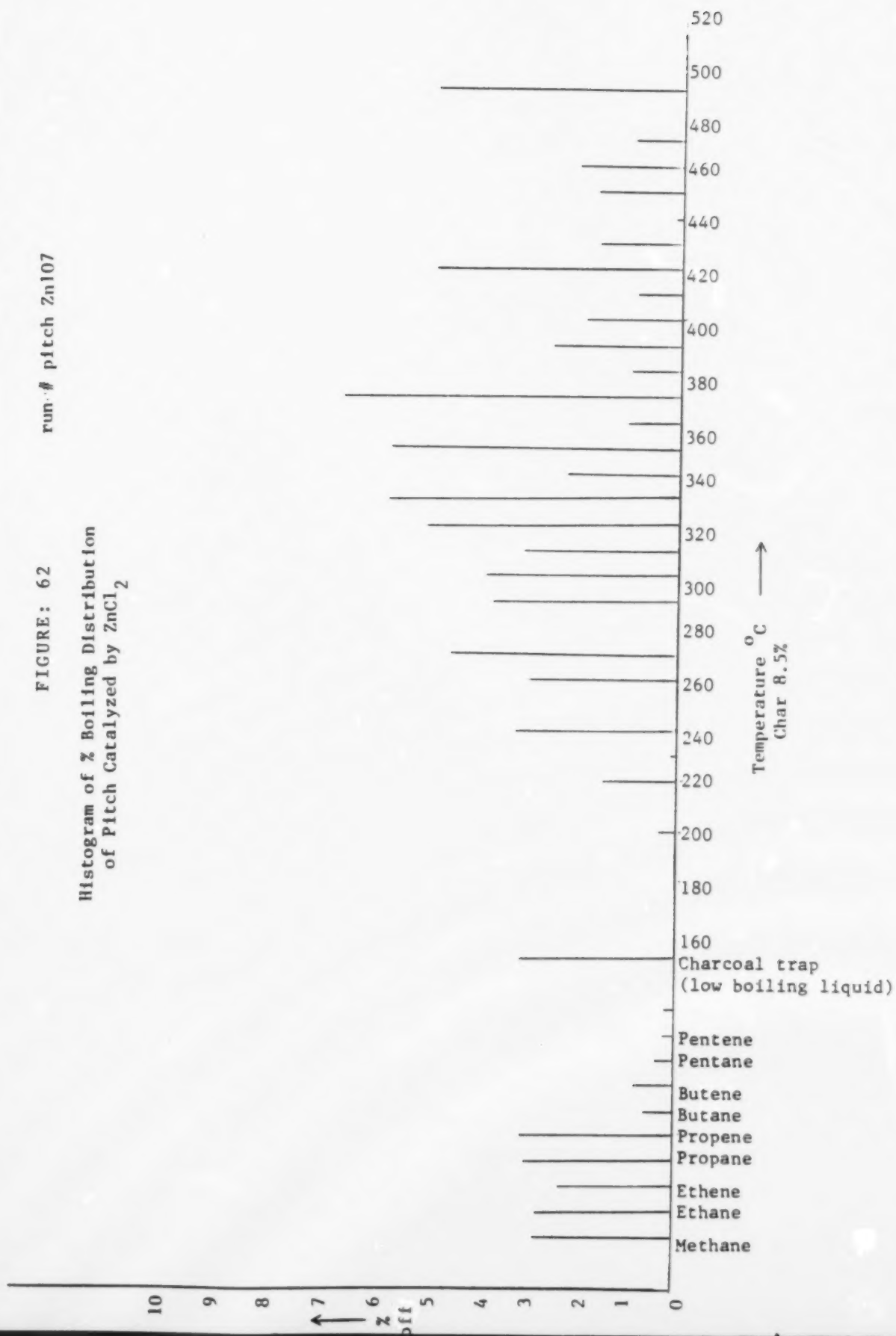
Histogram of % Boiling Distribution
of Pitch Catalyzed by ZnCl_2 

FIGURE: 63

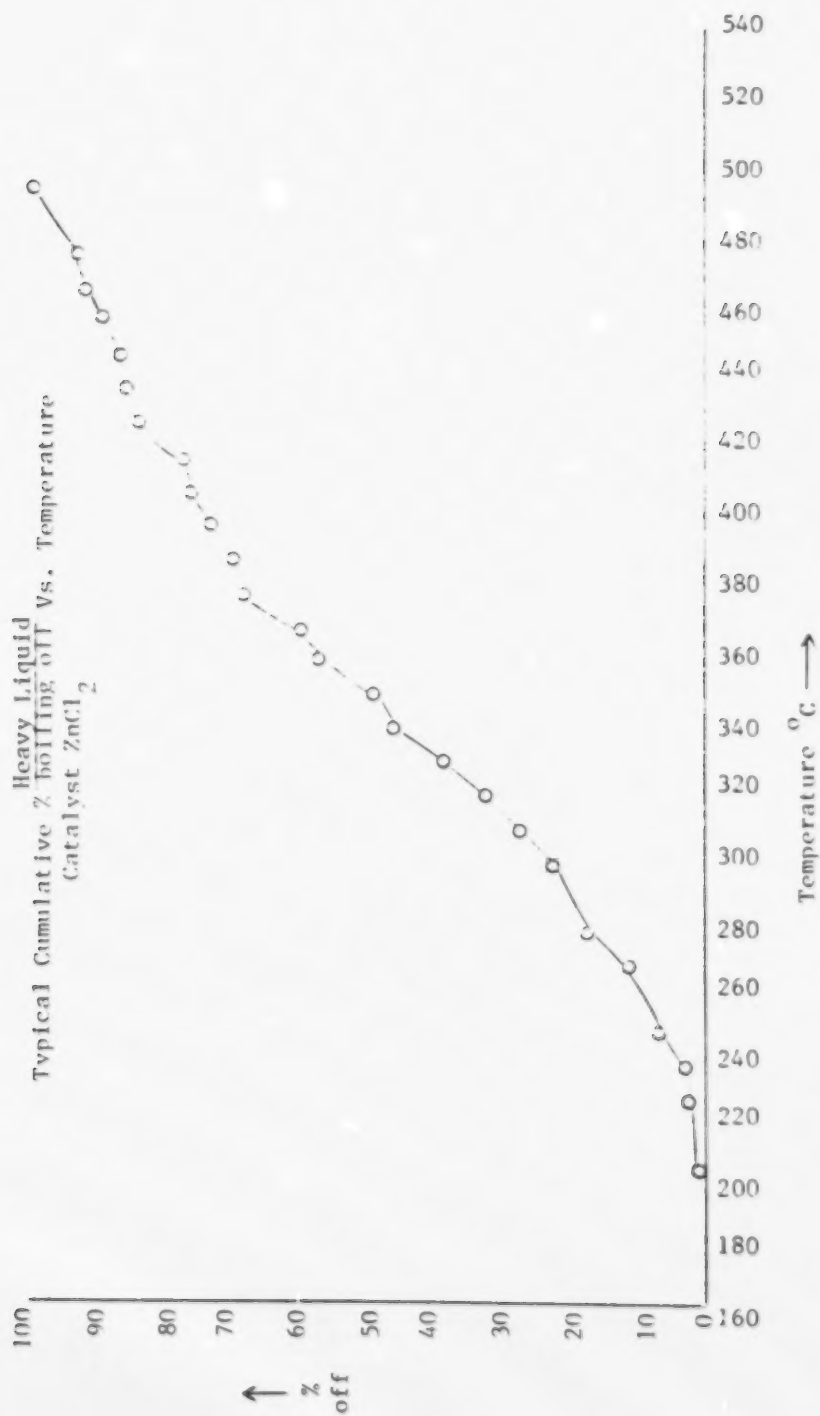


FIGURE: 64 Histogram of % Boiling Distribution
of Pitch Catalyzed by ZnCl_2

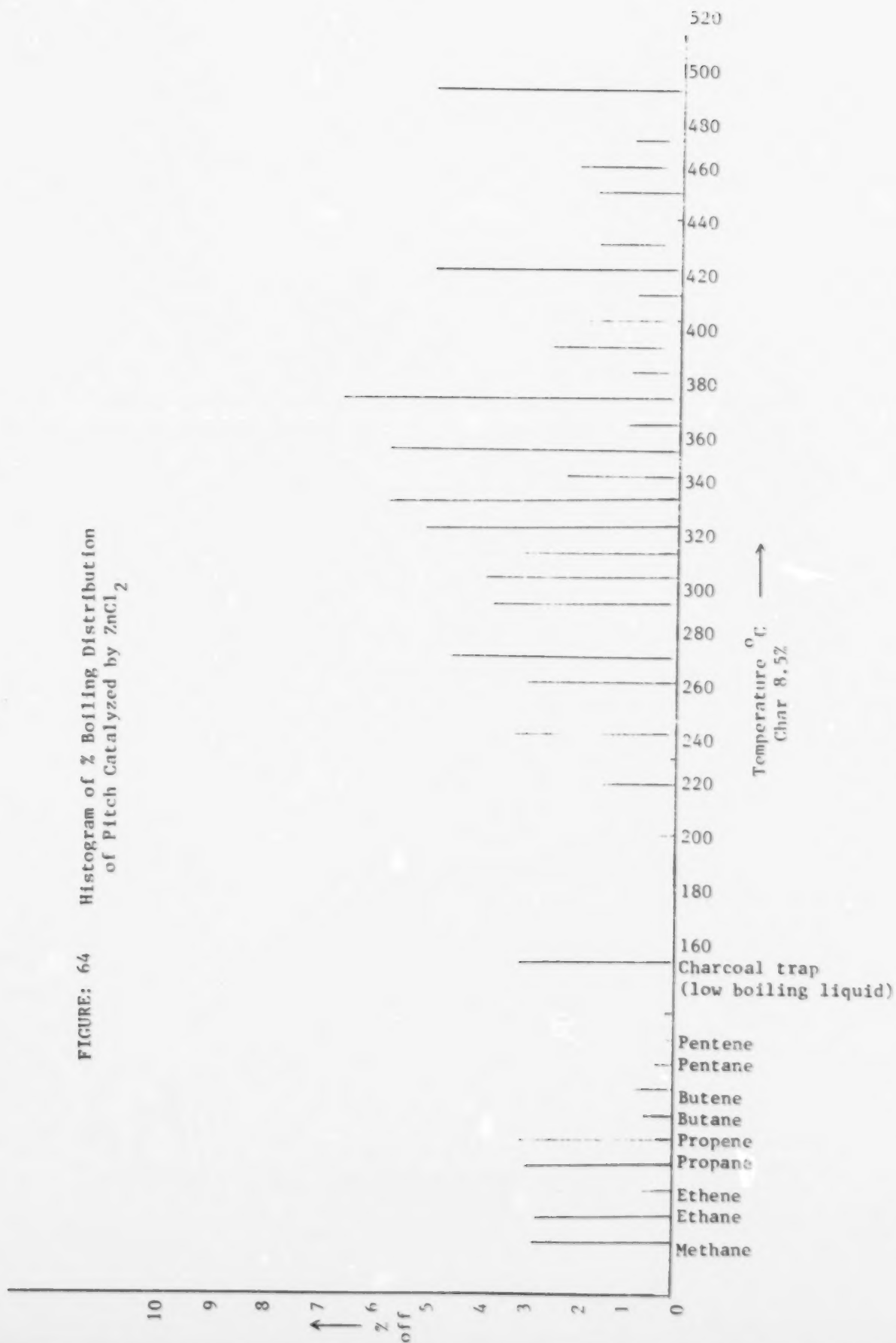


FIGURE: 65
Typical Cumulative % boiling off Vs. Temperature
Pitch without FHP

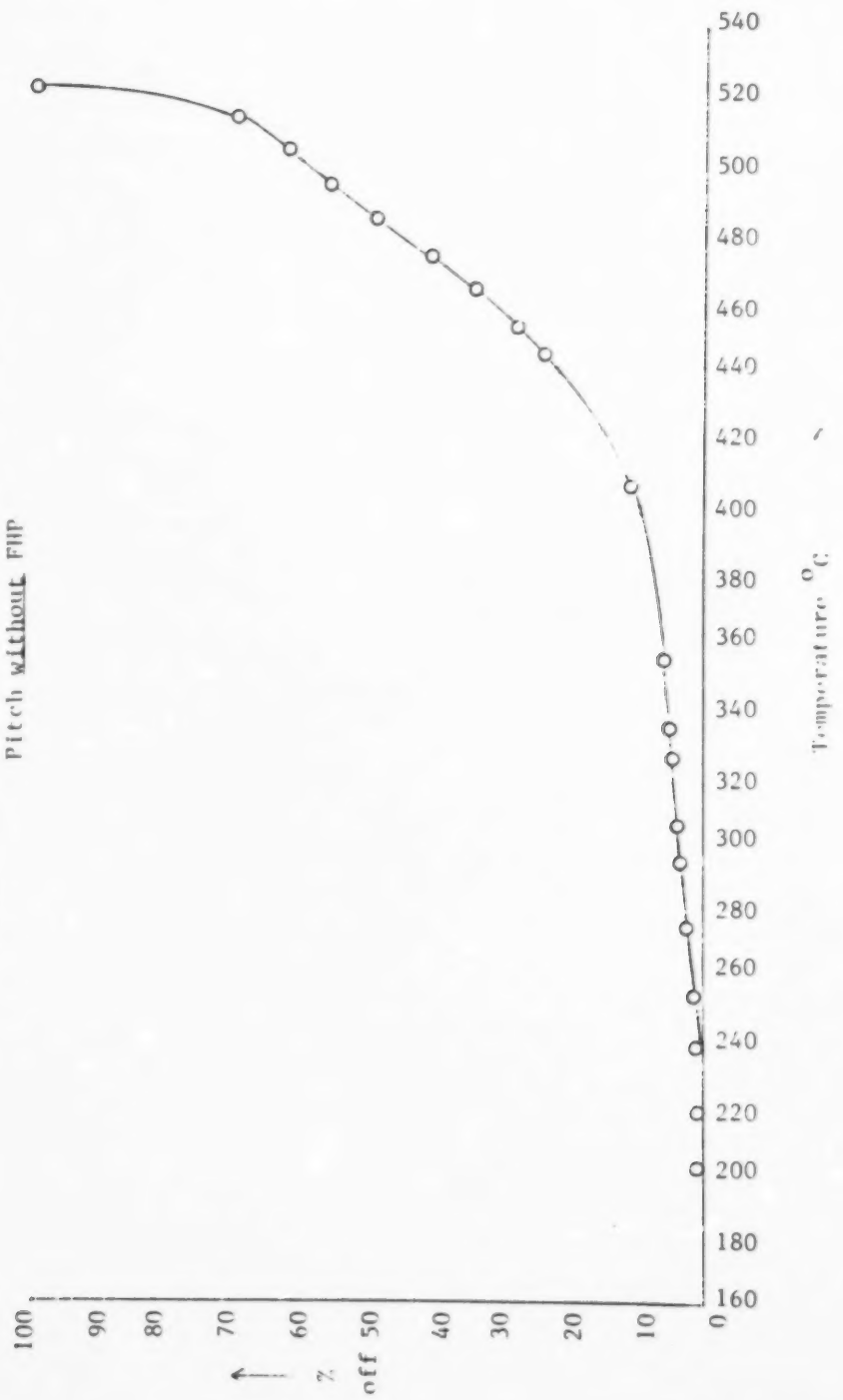
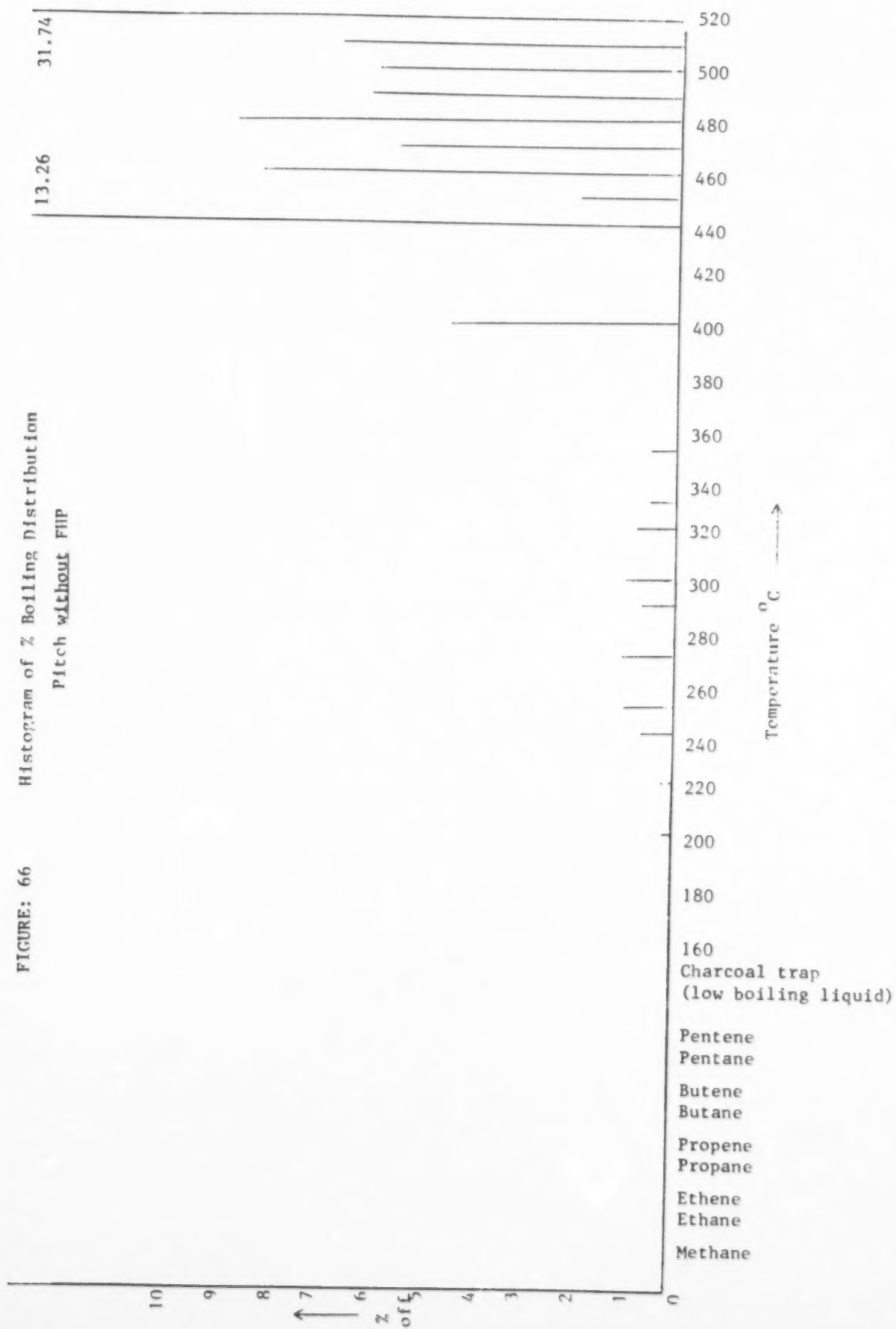


FIGURE: 66 Histogram of % Boiling Distribution
Pitch without FMP



SUMMARY OF ZINC CHLORIDE
CATALYZED FHP OF +525 °C
COLD LAKE PITCH

Tables A23 - A62

TABLE A23

Results of Experimental Measurements

Run No.	01	02
Catalyst type	NONE	NONE
Catalyst/pitch ratio m/m	---	---
Maximum temperature °C	666	559
Heating rate °C/sec	226	226
H ₂ pressure psi	1000	1000
residence time sec	3.95	3.95
mass pitch mg total	115.0	121.0
mass pitch mg C	94.3	99.2
<u>m %C of Pitch</u>		
C ₁	14.8	3.5
C ₂ 's	3.0	3.6
C ₃ 's	---	0.8
C ₄ 's	---	0.6
C ₅ 's	---	---
Other	---	---
Total Gas	17.8	8.5
<u>Liquids</u>		
Light Distillate	9.3	19.0
Heavy Distillate	---	---
Residue	---	---
TOTAL	---	---

TABLE A24

Results of Experimental Measurements

Run No.	03	04
Catalyst type	NONE	NONE
Catalyst/pitch ratio m/m	----	----
Maximum temperature °C	523	573
Heating rate °C/sec	178	190
H pressure psi	1000	1000
residence time sec	3.95	3.95
mass pitch mg total	124.0	147.0
mass pitch mg C	102.1	120.9
<u>m %C of Pitch</u>		
C	14.8	6.6
C ₁ 's	8.9	8.9
C ₂ 's	1.0	4.4
C ₃ 's	<0.1	0.5
C ₄ 's	---	0.6
C ₅	---	<0.1
Other	---	<0.1
Total Gas	24.7	21.0
<u>Liquids</u>		
Light Distillate	8.0	13.6
Heavy Distillate	20.2	24.7
Residue	39.4	30.1
TOTAL	92.3	89.4

TABLE A25

Results of Experimental Measurements

Run No.	05	13
Catalyst type	NONE	NONE
Catalyst/pitch ratio m/m	----	----
Maximum temperature °C	684	618
Heating rate °C/sec	249	285
H ₂ pressure psi	1000	500
residence time sec	3.95	2.00
mass pitch mg total	139.0	90.0
mass pitch mg C	114.4	74.1
<u>m %C of Pitch</u>		
C ₁	17.6	4.3
C ₂ 's	6.1	8.1
C ₃ 's	0.4	6.6
C ₄ 's	<0.1	0.7
C ₅ 's	0.1	2.2
Other	---	---
Total Gas	24.2	21.9
<u>Liquids</u>		
Light Distillate	6.6	11.3
Heavy Distillate	20.8	25.2
Residue	42.1	60.7
TOTAL	93.7	119.1

TABLE A26

Results of Experimental Measurements

Run No.	11	12
Catalyst type	NONE	NONE
Catalyst/pitch ratio m/m	----	----
Maximum temperature °C	630	642
Heating rate °C/sec	261	238
H ₂ pressure psi	1000	1000
residence time sec	3.95	3.95
mass pitch mg total	71.0	213.0
mass pitch mg C	58.4	175.3
<u>m %C of Pitch</u>		
C	7.9	14.1
C ₁ 's	10.4	7.4
C ₂ 's	6.2	1.1
C ₃ 's	1.1	0.2
C ₄ 's	1.1	0.3
C ₅	---	---
Other	---	---
Total Gas	26.7	22.9
<u>Liquids</u>		
Light Distillate	8.0	9.4
Heavy Distillate	20.4	19.7
Residue	13.7	3.8
TOTAL	68.8	55.4

TABLE A27

Results of Experimental Measurements

Run No.	14	15
Catalyst type	NONE	NONE
Catalyst/pitch ratio m/m	----	----
Maximum temperature °C	618	594
Heating rate °C/sec	285	213
H ₂ pressure psi	500	500
residence time sec	2.00	2.00
mass pitch mg total	104.0	97.0
mass pitch mg C	85.6	79.8
<u>m %C of Pitch</u>		
C	3.8	6.3
C ₁ 's	7.0	10.7
C ₂ 's	5.2	7.3
C ₃ 's	0.5	0.7
C ₄ 's	1.3	2.3
C ₅	---	---
Other	---	---
Total Gas	17.8	27.3
<u>Liquids</u>		
Light Distillate	9.8	11.4
Heavy Distillate	27.6	26.9
Residue	58.7	53.2
TOTAL	113.9	118.8

TABLE A28

Results of Experimental Measurements

Run No.	26	27
Catalyst type	ZnCl ₂	ZnCl ₂
Catalyst/pitch ratio m/m	0.64	0.61
Maximum temperature °C	535	554
Heating rate °C/sec	214	169
H ₂ pressure psi	1000	1000
residence time sec	3.90	3.90
mass pitch mg total	126.0	119.0
mass pitch mg C	103.3	97.6
<u>m %C of Pitch</u>		
C	---	---
C ₁	---	---
C ₂	---	---
C ₃	---	---
C ₄	---	---
C ₅	---	---
Other	---	---
Total Gas	---	---
<u>Liquids</u>		
Light Distillate	---	16.8
Heavy Distillate	---	1.8
Residue	---	---
TOTAL	---	---

TABLE A29

Results of Experimental Measurements

Run No.	28	29
Catalyst type	ZnCl ₂	ZnCl ₂
Catalyst/pitch ratio m/m	0.48	0.54
Maximum temperature °C	606	554
Heating rate °C/sec	261	202
H ₂ pressure psi	1000	1000
residence time sec	3.90	3.90
mass pitch mg total	119.0	121.0
mass pitch mg C	97.6	99.2
<u>m %C of Pitch</u>		
C ₁	10.0	0.4
C ₂ 's	7.1	5.6
C ₃ 's	0.1	1.9
C ₄ 's	<0.1	1.5
C ₅ 's	---	1.7
Other	---	---
Total Gas	17.1	11.1
<u>Liquids</u>		
Light Distillate	16.8	16.2
Heavy Distillate	1.2	1.9
Residue	---	---
TOTAL	---	---

TABLE A30

Results of Experimental Measurements

Run No.	30	31
Catalyst type	ZnCl ₂	ZnCl ₂
Catalyst/pitch ratio m/m	0.48	0.50
Maximum temperature °C	475	547
Heating rate °C/sec	166	226
H ₂ pressure psi	1000	1000
residence time sec	3.90	3.95
mass pitch mg total	135.0	133.0
mass pitch mg C	110.7	109.1
<u>m %C of Pitch</u>		
C ₁	2.2	2.5
C ₂ 's	0.5	1.8
C ₃ 's	---	---
C ₄ 's	---	---
C ₅ 's	---	---
Other	---	---
Total Gas	2.7	4.3
<u>Liquids</u>		
Light Distillate	16.8	15.6
Heavy Distillate	1.2	1.8
Residue	---	---
TOTAL	---	---

TABLE A31

Results of Experimental Measurements

Run No.	32	33
Catalyst type	ZnCl ₂	ZnCl ₂
Catalyst/pitch ratio m/m	0.68	0.71
Maximum temperature °C	618	487
Heating rate °C/sec	239	178
H ₂ pressure psi	1000	1000
residence time sec	3.95	3.95
mass pitch mg total	111.0	109.0
mass pitch mg C	91.0	89.4
<u>m %C of Pitch</u>		
C ₁	18.0	0.2
C ₂ 's	4.4	0.3
C ₃ 's	---	0.1
C ₄ 's	---	<0.1
C ₅ 's	---	---
Other	---	---
Total Gas	22.3	0.6
<u>Liquids</u>		
Light Distillate	10.9	12.8
Heavy Distillate	6.0	1.4
Residue	---	---
TOTAL	---	---

TABLE A32

Results of Experimental Measurements

Run No.	34	35
Catalyst type	ZnCl ₂	ZnCl ₂
Catalyst/pitch ratio m/m	0.55	0.51
Maximum temperature °C	487	463
Heating rate °C/sec	178	154
H ₂ pressure psi	1000	1000
residence time sec	3.95	3.95
mass pitch mg total	131.0	121.0
mass pitch mg C	107.4	99.2
<u>m %C of Pitch</u>		
C ₁	0.2	1.1
C ₂ 's	0.3	1.4
C ₃ 's	---	0.4
C ₄ 's	<0.1	0.2
C ₅ 's	---	0.2
Other	---	---
Total Gas	0.5	3.3
<u>Liquids</u>		
Light Distillate	14.1	17.0
Heavy Distillate	2.1	1.8
Residue	---	---
TOTAL	---	---

TABLE A33

Results of Experimental Measurements

Run No.	36	37
Catalyst type	ZnCl ₂	ZnCl ₂
Catalyst/pitch ratio m/m	0.66	0.58
Maximum temperature °C	559	487
Heating rate °C/sec	202	143
H ₂ pressure psi	1000	1000
residence time sec	3.95	3.95
mass pitch mg total	125.0	120.0
mass pitch mg C	102.5	98.4
<u>m %C of Pitch</u>		
C ₁	6.0	0.1
C ₂ 's	1.8	0.3
C ₃ 's	---	<0.1
C ₄ 's	---	<0.1
C ₅ 's	---	---
Other	---	---
Total Gas	7.8	0.4
<u>Liquids</u>		
Light Distillate	11.2	9.0
Heavy Distillate	2.4	3.2
Residue	---	---
TOTAL	---	---

TABLE A34

Results of Experimental Measurements

Run No.	38
Catalyst type	NONE
Catalyst/pitch ratio m/m	---
Maximum temperature °C	523
Heating rate °C/sec	202
H ₂ pressure psi	1000
residence time sec	3.95
mass pitch mg total	111.0
mass pitch mg C	91.0
<u>m %C of Pitch</u>	
C1	1.3
C2's	0.2
C ₃ 's	---
C ₄ 's	---
C ₅ 's	---
Other	---
Total Gas	1.5
<u>Liquids</u>	
Light Distillate	15.4
Heavy Distillate	---
Residue	---
TOTAL	---

TABLE A35

Results of Experimental Measurements

Run No.	Zn39	Zn40
Catalyst type	ZnCl ₂	ZnCl ₂
Catalyst/pitch ratio m/m	0.64	0.50
Maximum temperature °C	594	546
Heating rate °C/sec	166	166
H ₂ pressure psi	1000	1000
residence time sec	3.95	3.95
mass pitch mg total	121.0	127.0
mass pitch mg C	100.7	105.7
<u>m %C of Pitch</u>		
C ₁	5.6	3.0
C ₂ 's	6.8	4.8
C ₃ 's	3.5	11.1
C ₄ 's	1.9	1.3
C ₅ 's	0.3	2.1
Other	<0.1	0.2
Total Gas	18.1	22.5
<u>Liquids</u>		
Light Distillate	10.1	13.1
Heavy Distillate	---	---
Residue	---	---
TOTAL	---	---

TABLE A36

Results of Experimental Measurements

Run No.	Zn41	Zn42
Catalyst type	ZnCl ₂	ZnCl ₂
Catalyst/pitch ratio m/m	0.62	0.54
Maximum temperature °C	595	630
Heating rate °C/sec	178	190
H ₂ pressure psi	1000	1000
residence time sec	3.95	10.85
mass pitch mg total	118.0	131.0
mass pitch mg C	97.1	107.8
<u>m %C of Pitch</u>		
C ₁	16.3	11.2
C ₁ 's	13.1	8.4
C ₂	1.4	1.9
C ₂ 's	<0.1	0.2
C ₃	<0.1	0.2
C ₃ 's	<0.1	<0.1
C ₄	<0.1	<0.1
C ₄ 's	<0.1	<0.1
C ₅	<0.1	<0.1
Other	<0.1	<0.1
Total Gas	30.8	21.9
<u>Liquids</u>		
Light Distillate	10.3	8.3
Heavy Distillate	20.1	22.4
Residue	20.3	21.3
TOTAL	81.5	73.9

TABLE A37

Results of Experimental Measurements

Run No.	Zn43	Zn44
Catalyst type	ZnCl ₂	ZnCl ₂
Catalyst/pitch ratio m/m	0.52	0.49
Maximum temperature °C	606	573
Heating rate °C/sec	190	202
H ₂ pressure psi	1000	1000
residence time sec	10.85	10.85
mass pitch mg total	128.0	120.0
mass pitch mg C	105.3	98.8
<u>m %C of Pitch</u>		
C ₁	13.4	11.4
C ₂ 's	7.5	10.3
C ₃ 's	1.2	3.3
C ₄ 's	<0.1	0.4
C ₅ 's	0.1	1.6
Other	<0.1	0.2
Total Gas	22.2	27.2
<u>Liquids</u>		
Light Distillate	8.1	11.0
Heavy Distillate	20.2	20.0
Residue	18.7	20.5
TOTAL	69.2	78.6

TABLE A38

Results of Experimental Measurements

Run No.	Zn45	Zn46
Catalyst type	ZnCl ₂	ZnCl ₂
Catalyst/pitch ratio m/m	0.48	0.51
Maximum temperature °C	784	618
Heating rate °C/sec	285	237
H ₂ pressure psi	1000	1000
residence time sec	3.95	3.95
mass pitch mg total	122.0	122.0
mass pitch mg C	100.4	100.4
<u>m %C of Pitch</u>		
C ₁	21.6	17.0
C ₂ 's	3.5	6.3
C ₃ 's	0.2	0.5
C ₄ 's	---	0.1
C ₅ 's	---	<0.1
Other	---	---
Total Gas	25.3	23.8
<u>Liquids</u>		
Light Distillate	5.0	9.7
Heavy Distillate	26.7	19.2
Residue	25.8	22.7
TOTAL	82.8	75.5

TABLE A39

Results of Experimental Measurements

Run No.	Zn47	Zn48
Catalyst type	ZnCl ₂	ZnCl ₂
Catalyst/pitch ratio m/m	0.57	0.61
Maximum temperature °C	736	701
Heating rate °C/sec	285	249
H ₂ pressure psi	1000	1000
residence time sec	3.95	10.85
mass pitch mg total	122.0	131.0
mass pitch mg C	100.4	107.8
<u>m %C of Pitch</u>		
C ₁	19.6	10.8
C ₁ 's	1.6	7.6
C ₂	0.2	1.1
C ₂ 's	---	<0.1
C ₃	<0.1	0.1
C ₃ 's	---	<0.1
C ₄	---	---
C ₄ 's	---	---
C ₅	---	---
C ₅ 's	---	---
Other	---	---
Total Gas	21.4	19.6
<u>Liquids</u>		
Light Distillate	8.4	10.5
Heavy Distillate	24.4	18.5
Residue	16.8	20.6
TOTAL	71.0	69.2

TABLE A40

Results of Experimental Measurements

Run No.	Zn49	Zn50
Catalyst type	ZnCl ₂	ZnCl ₂
Catalyst/pitch ratio m/m	0.55	0.64
Maximum temperature °C	642	701
Heating rate °C/sec	190	237
H ₂ pressure psi	1000	1000
residence time sec	10.85	10.85
mass pitch mg total	134.0	131.0
mass pitch mg C	110.3	107.8
<u>m %C of Pitch</u>		
C ₁	11.8	10.1
C ₂ 's	3.2	1.7
C ₃ 's	0.2	0.1
C ₄ 's	---	---
C ₅ 's	---	---
Other	---	---
Total Gas	15.2	11.8
<u>Liquids</u>		
Light Distillate	8.7	8.2
Heavy Distillate	20.7	20.1
Residue	14.2	15.0
TOTAL	58.8	55.2

TABLE A41

Results of Experimental Measurements

Run No.	Zn51
Catalyst type	ZnCl ₂
Catalyst/pitch ratio m/m	0.64
Maximum temperature °C	606
Heating rate °C/sec	237
H ₂ pressure psi	1000
residence time sec	10.85
mass pitch mg total	120.0
mass pitch mg C	98.8
<u>m %C of Pitch</u>	
C1	10.7
C2's	4.4
C ₃ 's	0.3
C ₄ 's	---
C ₅ 's	---
Other	---
Total Gas	15.5
<u>Liquids</u>	
Light Distillate	7.4
Heavy Distillate	16.4
Residue	29.1
TOTAL	68.4

TABLE A42

Results of Experimental Measurements

Run No.	Zn64	Zn65
Catalyst type	ZnCl ₂	ZnCl ₂
Catalyst/pitch ratio m/m	1.84	1.02
Maximum temperature °C	594	570
Heating rate °C/sec	274	261
H ₂ pressure psi	1000	1000
residence time sec	3.95	4.88
mass pitch mg total	57.0	62.0
mass pitch mg C	46.7	51.0
<u>m %C of Pitch</u>		
C	13.4	---
C ₁ 's	15.0	---
C ₂ 's	3.1	---
C ₃ 's	0.3	---
C ₄ 's	0.4	---
C ₅	---	---
Other	---	---
Total Gas	32.2	00.0
<u>Liquids</u>		
Light Distillate	11.5	10.6
Heavy Distillate	40.9	22.2
Residue	15.1	7.6
TOTAL	99.7	40.4

TABLE A43

Results of Experimental Measurements

Run No.	Zn66	Zn67
Catalyst type	ZnCl ₂	ZnCl ₂
Catalyst/pitch ratio m/m	0.68	0.48
Maximum temperature °C	475	1117
Heating rate °C/sec	190	261
H ₂ pressure psi	1000	1000
residence time sec	3.95	3.95
mass pitch mg total	178.0	217.0
mass pitch mg C	146.5	178.6
<u>m %C of Pitch</u>		
C	7.9	17.4
1		
C 's	11.6	0.7
2		
C 's	6.1	<0.1
3		
C 's	0.3	---
4		
C 's	0.6	---
5		
Other	---	---
Total Gas	26.4	18.1
<u>Liquids</u>		
Light Distillate	14.4	3.6
Heavy Distillate	37.0	12.8
Residue	9.1	18.3
TOTAL	87.0	52.8

TABLE A44

Results of Experimental Measurements

Run No.	Zn68	Zn71
Catalyst type	ZnCl ₂	ZnCl ₂
Catalyst/pitch ratio m/m	0.95	1.43
Maximum temperature °C	570	499
Heating rate °C/sec	---	238
H ₂ pressure psi	500	500
residence time sec	2.00	2.00
mass pitch mg total	109.0	105.0
mass pitch mg C	89.7	86.4
<u>m %C of Pitch</u>		
C ₁	12.2	4.0
C ₂ 's	13.2	7.0
C ₃ 's	2.8	5.2
C ₄ 's	<0.1	0.4
C ₅ 's	0.3	1.1
Other	<0.1	<0.1
Total Gas	28.6	17.8
<u>Liquids</u>		
Light Distillate	8.7	11.1
Heavy Distillate	51.3	45.4
Residue	14.4	7.1
TOTAL	102.9	80.0

TABLE A45

Results of Experimental Measurements

Run No.	Zn69	Zn70
Catalyst type	ZnCl ₂	ZnCl ₂
Catalyst/pitch ratio m/m	1.14	1.32
Maximum temperature °C	606	641
Heating rate °C/sec	238	238
H ₂ pressure psi	500	500
residence time sec	2.00	2.00
mass pitch mg total	121.0	111.0
mass pitch mg C	99.6	91.4
<u>m %C of Pitch</u>		
C	0.8	3.9
C ₁ 's	1.3	7.2
C ₂ 's	1.1	5.3
C ₃ 's	0.2	0.6
C ₄ 's	0.7	2.2
C ₅	---	---
Other	---	---
Total Gas	4.1	19.1
<u>Liquids</u>		
Light Distillate	1.9	7.6
Heavy Distillate	31.9	56.1*
Residue	---	17.1
TOTAL	---	---

TABLE A46

Results of Experimental Measurements

Run No.	Zn72	Zn73
Catalyst type	ZnCl ₂	ZnCl ₂
Catalyst/pitch ratio m/m	1.40	1.40
Maximum temperature °C	499	511
Heating rate °C/sec	190	190
H ₂ pressure psi	500	500
residence time sec	2.00	2.00
mass pitch mg total	99.0	91.0
mass pitch mg C	81.5	74.9
<u>m %C of Pitch</u>		
C	---	4.2
1	---	7.2
C 's	---	5.4
2	---	0.7
C 's	---	1.9
3	---	<0.1
C 's	---	
4	---	
C 's	---	
5	---	
Other	---	
Total Gas	00.0	19.4
<u>Liquids</u>		
Light Distillate	10.9	13.1
Heavy Distillate	36.7	31.4
Residue	10.3	9.1
TOTAL	---	73.0

TABLE A47

Results of Experimental Measurements

Run No.	Zn77	Zn78
Catalyst type	ZnCl ₂	ZnCl ₂
Catalyst/pitch ratio m/m	2.80	2.82
Maximum temperature °C	630	546
Heating rate °C/sec	238	190
H ₂ pressure psi	1000	1000
residence time sec	3.95	3.95
mass pitch mg total	49.8	52.4
mass pitch mg C	40.8	43.1
<u>m %C of Pitch</u>		
C	4.6	11.8
C ₁ 's	6.2	12.2
C ₂ 's	5.4	1.2
C ₃ 's	1.0	0.1
C ₄ 's	2.1	<0.1
C ₅	---	---
Other	---	---
Total Gas	19.3	25.5
<u>Liquids</u>		
Light Distillate	6.1	6.0
Heavy Distillate	---	---
Residue	---	---
TOTAL	---	---

TABLE A48

Results of Experimental Measurements

Run No.	Zn79	Zn80
Catalyst type	ZnCl ₂	ZnCl ₂
Catalyst/pitch ratio m/m	2.82	2.13
Maximum temperature °C	618	511
Heating rate °C/sec	332	238
H ₂ pressure psi	1000	1000
residence time sec	3.95	3.95
mass pitch mg total	52.4	57.8
mass pitch mg C	43.1	47.6
<u>m %C of Pitch</u>		
C	9.7	3.7
C ₁ 's	11.6	5.4
C ₂ 's	5.6	5.8
C ₃ 's	0.8	1.6
C ₄ 's	1.3	1.7
C ₅	---	---
Other	---	---
Total Gas	28.9	18.2
<u>Liquids</u>		
Light Distillate	3.0	7.6
Heavy Distillate	---	47.9
Residue	---	10.9
TOTAL	---	84.6

TABLE A49

Results of Experimental Measurements

Run No.	Zn81	Zn82
Catalyst type	ZnCl ₂	ZnCl ₂
Catalyst/pitch ratio m/m	2.13	2.08
Maximum temperature °C	641	737
Heating rate °C/sec	285	285
H ₂ pressure psi	1000	1000
residence time sec	3.95	3.95
mass pitch mg total	67.4	59.4
mass pitch mg C	55.5	48.9
<u>m %C of Pitch</u>		
C	29.0	26.3
C ₁ 's	3.5	7.2
C ₂ 's	0.1	0.2
C ₃ 's	---	---
C ₄ 's	---	---
C ₅ 's	<0.1	---
Other	---	---
Total Gas	32.6	33.7
<u>Liquids</u>		
Light Distillate	6.5	5.9
Heavy Distillate	---	---
Residue	---	---
TOTAL	---	---

TABLE A50

Results of Experimental Measurements

Run No.	Zn83	Zn84
Catalyst type	ZnCl ₂	ZnCl ₂
Catalyst/pitch ratio m/m	2.46	2.46
Maximum temperature °C	475	618
Heating rate °C/sec	190	214
H ₂ pressure psi	1000	1000
residence time sec	3.95	3.95
mass pitch mg total	58.3	57.5
mass pitch mg C	48.0	47.3
<u>m %C of Pitch</u>		
C	1.0	6.1
1		
C 's	1.7	8.5
2		
C 's	2.2	4.9
3		
C 's	0.8	0.6
4		
C 's	0.8	0.9
5		
Other	---	---
Total Gas	6.6	21.0
<u>Liquids</u>		
Light Distillate	6.7	8.7
Heavy Distillate	---	---
Residue	9.2	8.7
TOTAL	---	---

TABLE A51

Results of Experimental Measurements

Run No.	Zn85	Zn86
Catalyst type	ZnCl ₂	ZnCl ₂
Catalyst/pitch ratio m/m	2.46	2.12
Maximum temperature °C	713	582
Heating rate °C/sec	261	238
H ₂ pressure psi	1000	1000
residence time sec	3.95	3.95
mass pitch mg total	56.6	56.1
mass pitch mg C	46.6	46.2
<u>m %C of Pitch</u>		
C ₁	33.0	13.0
C ₂ 's	3.9	16.0
C ₃ 's	0.2	4.4
C ₄ 's	---	0.7
C ₅ 's	<0.1	0.7
Other	---	---
Total Gas	37.6	34.8
<u>Liquids</u>		
Light Distillate	2.8	6.1
Heavy Distillate	67.9	35.8
Residue	---	17.5
TOTAL	---	94.2

TABLE A52

Results of Experimental Measurements

Run No.	Zn87	Zn88
Catalyst type	ZnCl ₂	ZnCl ₂
Catalyst/pitch ratio m/m	2.12	2.12
Maximum temperature °C	606	511
Heating rate °C/sec	238	238
H ₂ pressure psi	1000	1000
residence time sec	3.95	3.95
mass pitch mg total	49.3	49.3
mass pitch mg C	40.6	40.6
<u>m %C of Pitch</u>		
C ₁	6.9	3.1
C ₂ 's	10.5	5.2
C ₃ 's	8.9	5.7
C ₄ 's	2.0	1.5
C ₅ 's	2.6	2.1
Other	---	---
Total Gas	30.8	17.7
<u>Liquids</u>		
Light Distillate	11.6	9.4
Heavy Distillate	---	---
Residue	21.2	22.4
TOTAL	---	---

TABLE A53

Results of Experimental Measurements

Run No.	Zn89
Catalyst type	ZnCl ₂
Catalyst/pitch ratio m/m	0.97
Maximum temperature °C	511
Heating rate °C/sec	237
H ₂ pressure psi	1000
residence time sec	3.95
mass pitch mg total	59.0
mass pitch mg C	48.6
<u>m %C of Pitch</u>	
C ₁	3.7
C ₁ 's	5.9
C ₂	6.3
C ₃ 's	1.1
C ₄	<0.1
C ₅ 's	<0.1
Other	<0.1
Total Gas	17.0
<u>Liquids</u>	
Light Distillate	8.0
Heavy Distillate	83.0
Residue	11.1
TOTAL	119.1

TABLE A54

Results of Experimental Measurements

Run No.	Zn90	Zn93
Catalyst type	ZnCl ₂	ZnCl ₂
Catalyst/pitch ratio m/m	0.93	0.52
Maximum temperature °C	523	490
Heating rate °C/sec	237	237
H ₂ pressure psi	1000	250
residence time sec	3.95	4.07
mass pitch mg total	55.0	52.0
mass pitch mg C	45.3	42.8
<u>m %C of Pitch</u>		
C ₁	3.9	1.7
C ₂ 's	4.3	2.0
C ₃ 's	6.2	2.0
C ₄ 's	1.5	1.0
C ₅ 's	0.9	1.2
Other	<0.1	1.2
Total Gas	16.8	9.1
<u>Liquids</u>		
Light Distillate	2.7	3.9
Heavy Distillate	69.3	76.6
Residue	7.2	8.5
TOTAL	96.0	96.8

TABLE A55

Results of Experimental Measurements

Run No.	Zn91	Zn92
Catalyst type	ZnCl ₂	ZnCl ₂
Catalyst/pitch ratio m/m	0.67	0.67
Maximum temperature °C	558	523
Heating rate °C/sec	285	237
H ₂ pressure psi	1000	500
residence time sec	3.95	4.88
mass pitch mg total	54.0	51.0
mass pitch mg C	44.4	42.0
<u>m %C of Pitch</u>		
C	3.6	4.0
C ₁ 's	5.9	5.3
C ₂ 's	5.9	5.2
C ₃ 's	1.2	0.5
C ₄ 's	1.0	<0.1
C ₅	<0.1	<0.1
Other	<0.1	<0.1
Total Gas	17.6	15.0
<u>Liquids</u>		
Light Distillate	6.7	31.9
Heavy Distillate	64.4*	40.3
Residue	11.3	9.9
TOTAL	100.0	97.1

TABLE A56

Results of Experimental Measurements

Run No.	Zn94	Zn95
Catalyst type	ZnCl ₂	ZnCl ₂
Catalyst/pitch ratio m/m	0.54	0.90
Maximum temperature °C	523	510
Heating rate °C/sec	214	237
H ₂ pressure psi	1400	1000
residence time sec	4.02	2.5
mass pitch mg total	50.0	53.0
mass pitch mg C	41.2	43.6
<u>m %C of Pitch</u>		
C	3.6	4.6
1		
C's	5.6	7.9
2		
C's	6.7	8.0
3		
C's	2.4	2.2
4		
C's	0.9	0.5
5		
Other	0.9	0.9
Total Gas	20.1	24.1
<u>Liquids</u>		
Light Distillate	9.7	4.5
Heavy Distillate	61.0	49.8
Residue	12.0	13.0
TOTAL	102.8	91.3

TABLE A57

Results of Experimental Measurements

Run No.	Zn96	Zn97
Catalyst type	ZnCl ₂	ZnCl ₂
Catalyst/pitch ratio m/m	0.93	0.46
Maximum temperature °C	594	333
Heating rate °C/sec	237	190
H ₂ pressure psi	1000	1000
residence time sec	10.85	3.95
mass pitch mg total	48.0	52.0
mass pitch mg C	39.5	42.8
<u>m %C of Pitch</u>		
C ₁	6.0	---
C ₂ 's	8.8	---
C ₃ 's	4.8	---
C ₄ 's	0.6	---
C ₅ 's	0.1	---
Other	<0.1	---
Total Gas	20.3	00.0
<u>Liquids</u>		
Light Distillate	5.2	1.1
Heavy Distillate	54.9	4.3
Residue	10.5	---
TOTAL	90.9	---

TABLE A58

Results of Experimental Measurements

Run No.	Zn98	Zn99
Catalyst type	ZnCl ₂	ZnCl ₂
Catalyst/pitch ratio m/m	0.50	0.90
Maximum temperature °C	452	559
Heating rate °C/sec	119	119
H ₂ pressure psi	1000	1000
residence time sec	3.95	3.95
mass pitch mg total	56.0	55.0
mass pitch mg C	46.1	45.3
<u>m %C of Pitch</u>		
C	0.1	2.3
1		
C's	0.1	4.1
2		
C's	0.3	4.9
3		
C's	0.5	1.2
4		
C's	0.2	1.7
5		
Other	<0.1	0.5
Total Gas	1.2	14.7
<u>Liquids</u>		
Light Distillate	1.3	4.8
Heavy Distillate	30.6	57.2
Residue	29.5	12.9
TOTAL	67.7	89.6

TABLE A59

Results of Experimental Measurements

Run No.	Zn100	Zn101
Catalyst type	ZnCl ₂	ZnCl ₂
Catalyst/pitch ratio m/m	0.64	0.90
Maximum temperature °C	510	547
Heating rate °C/sec	166	309
H ₂ pressure psi	1000	1000
residence time sec	3.95	3.95
mass pitch mg total	47.0	53.0
mass pitch mg C	38.7	43.6
<u>m %C of Pitch</u>		
C ₁	0.7	11.0
C ₂ 's	1.4	11.9
C ₃ 's	2.0	4.7
C ₄ 's	1.0	1.0
C ₅ 's	0.9	0.4
Other	0.8	0.3
Total Gas	6.8	29.3
<u>Liquids</u>		
Light Distillate	3.6	5.5
Heavy Distillate	42.7	41.8
Residue	---	10.5
TOTAL	---	87.1

TABLE A60

Results of Experimental Measurements

Run No.	Zn102	Zn104
Catalyst type	ZnCl ₂	ZnCl ₂
Catalyst/pitch ratio m/m	0.67	0.55
Maximum temperature °C	547	416
Heating rate °C/sec	237	119
H ₂ pressure psi	1000	500
residence time sec	3.95	4.88
mass pitch mg total	51.0	51.0
mass pitch mg C	42.0	42.0
<u>m %C of Pitch</u>		
C ₁	4.8	0.5
C ₂ 's	6.0	1.1
C ₃ 's	1.9	1.7
C ₄ 's	0.2	0.4
C ₅ 's	0.1	<0.1
Other	<0.1	<0.1
Total Gas	13.0	3.7
<u>Liquids</u>		
Light Distillate	6.1	---
Heavy Distillate	53.9	73.9
Residue	12.5	12.9
TOTAL	85.5	---

TABLE A61

Results of Experimental Measurements

Run No.	Zn103	Zn107
Catalyst type	ZnCl ₂	ZnCl ₂
Catalyst/pitch ratio m/m	0.90	0.57
Maximum temperature °C	701	512
Heating rate °C/sec	237	237
H ₂ pressure psi	1000	500
residence time sec	3.95	4.88
mass pitch mg total	57.0	51.0
mass pitch mg C	46.9	42.0
<u>m %C of Pitch</u>		
C ₁	27.9	2.7
C ₂ 's	7.2	5.2
C ₃ 's	1.2	6.0
C ₄ 's	1.5	1.4
C ₅ 's	<0.1	0.6
Other	<0.1	0.2
Total Gas	37.8	16.1
<u>Liquids</u>		
Light Distillate	8.1	3.1
Heavy Distillate	37.2	73.5
Residue	12.1	8.5
TOTAL	95.2	101.2

TABLE A62

Results of Experimental Measurements

Run No.	Zn105	Zn106
Catalyst type	ZnCl ₂	ZnCl ₂
Catalyst/pitch ratio m/m	0.54	0.62
Maximum temperature °C	499	416
Heating rate °C/sec	214	119
H ₂ pressure psi	500	500
residence time sec	4.88	4.88
mass pitch mg total	50.0	52.0
mass pitch mg C	41.6	43.3
<u>m %C of Pitch</u>		
C ₁	2.1	1.4
C ₂ 's	3.9	2.9
C ₃ 's	4.6	3.6
C ₄ 's	1.2	1.0
C ₅ 's	0.2	0.2
Other	<0.1	<0.1
Total Gas	12.0	9.1
<u>Liquids</u>		
Light Distillate	1.7	---
Heavy Distillate	59.1	54.4
Residue	10.6	9.4
TOTAL	83.4	72.9

V.3 Results of SnCl_4
Catalyzed Experiments

Table 23

Run #	pitch SnO1
Catalyst/pitch ratio m/m	= 1.695
Maximum Temperature oC	= 523
Heating Rate oC sec.	= 237
H2 pressure psi	= 1,000
residence time sec.	= 3.95
mass pitch mg	= 74.6
mass pitch mg C	= 61.5
mass catalyst mg total	= 126.4

	% of total C
methane	4.2
ethane	3.5
ethene	0.6
propane	3.8
propene	1.9
butane	1.3
butene	1.3
pentane	0.6
pentene	—
other	—
BTX liquid (light)	6.2
liquid (heavy)	53.2
*Char (residue)	21.8

* Char is whatever is left in the boat after the flash and analyzed by oxidation with oxidation and measuring CO₂ formed by gas-chromatography.

Table 24

Run #	pitch SnO ₂
Catalyst/pitch ratio m/m	= 1.695
Maximum Temperature °C	= 523
Heating Rate °C sec.	= 237
H ₂ pressure psi	= 1,000
residence time sec.	= 3.95
mass pitch mg	= 60.1
mass pitch mg C	= 49.5
mass catalyst mg total	= 101.9

	% of total C
methane	5.1
ethane	3.8
ethene	0.6
propane	4.3
propene	2.0
butane	1.4
butene	1.0
pentane	0.4
pentene	—
other	—
BTX liquid (light)	6.4
liquid (heavy)	58.0
*Char (residue)	22.4

* Char is whatever is left in the boat after the flash

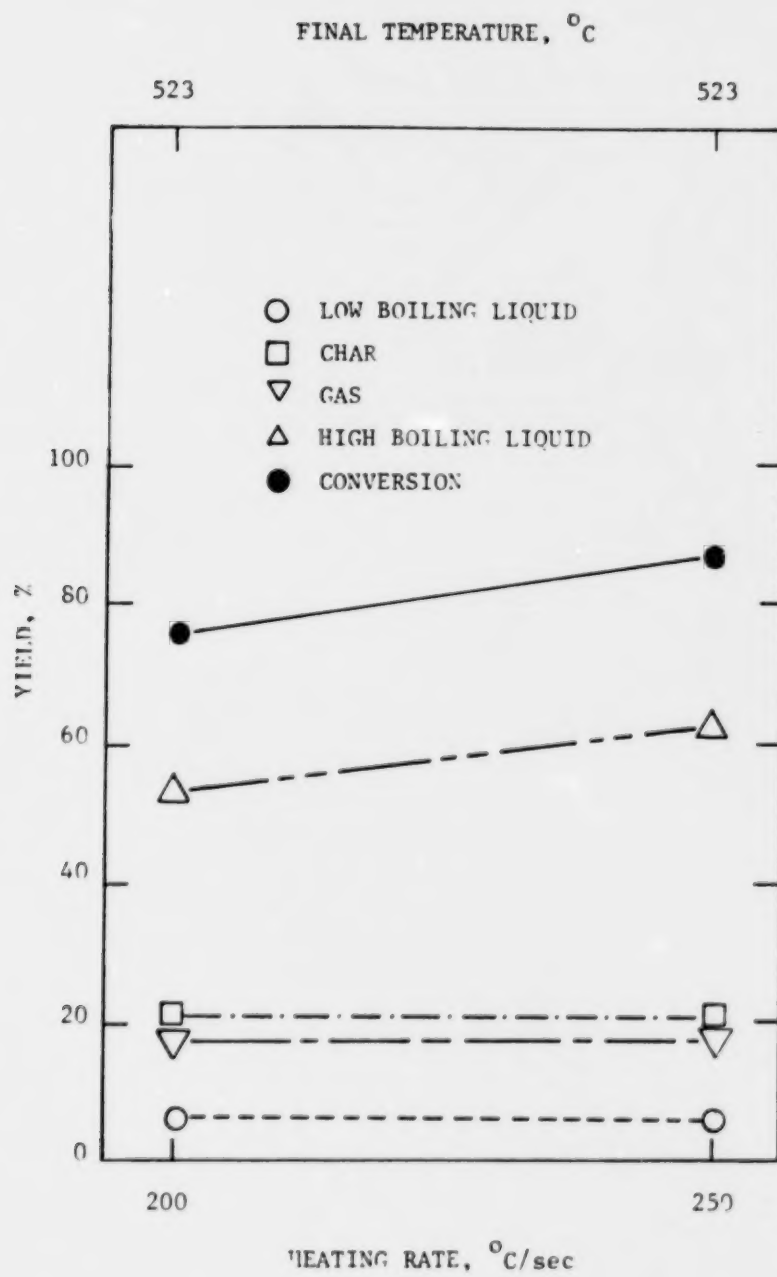


FIGURE 67: A plot of yield versus heating rate. Run No. Pitch Sn01 and Sn02.

Figure 68: Histogram of % Boiling Distribution
of Pitch Catalyzed by SnCl_4
Run # Sn01

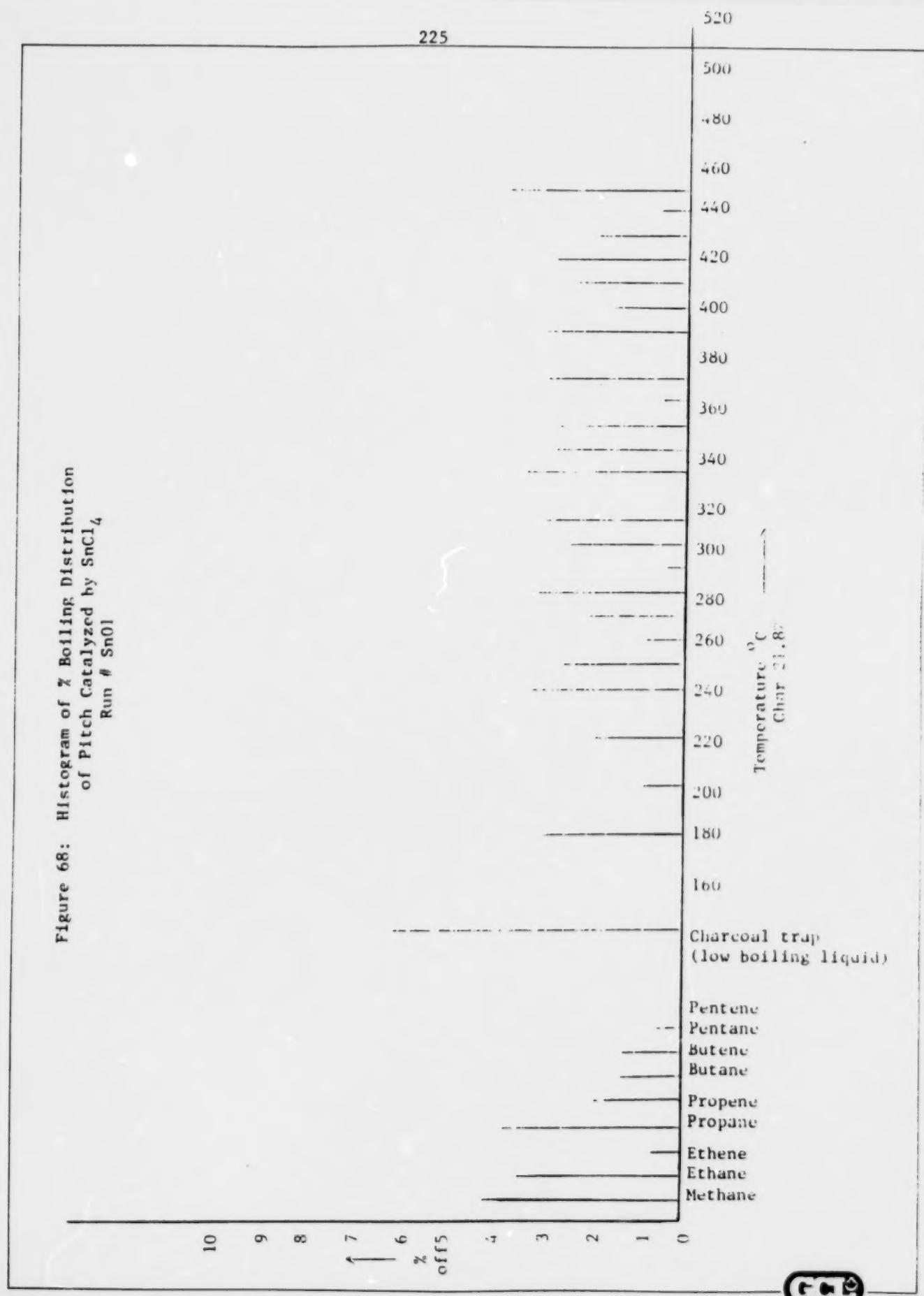
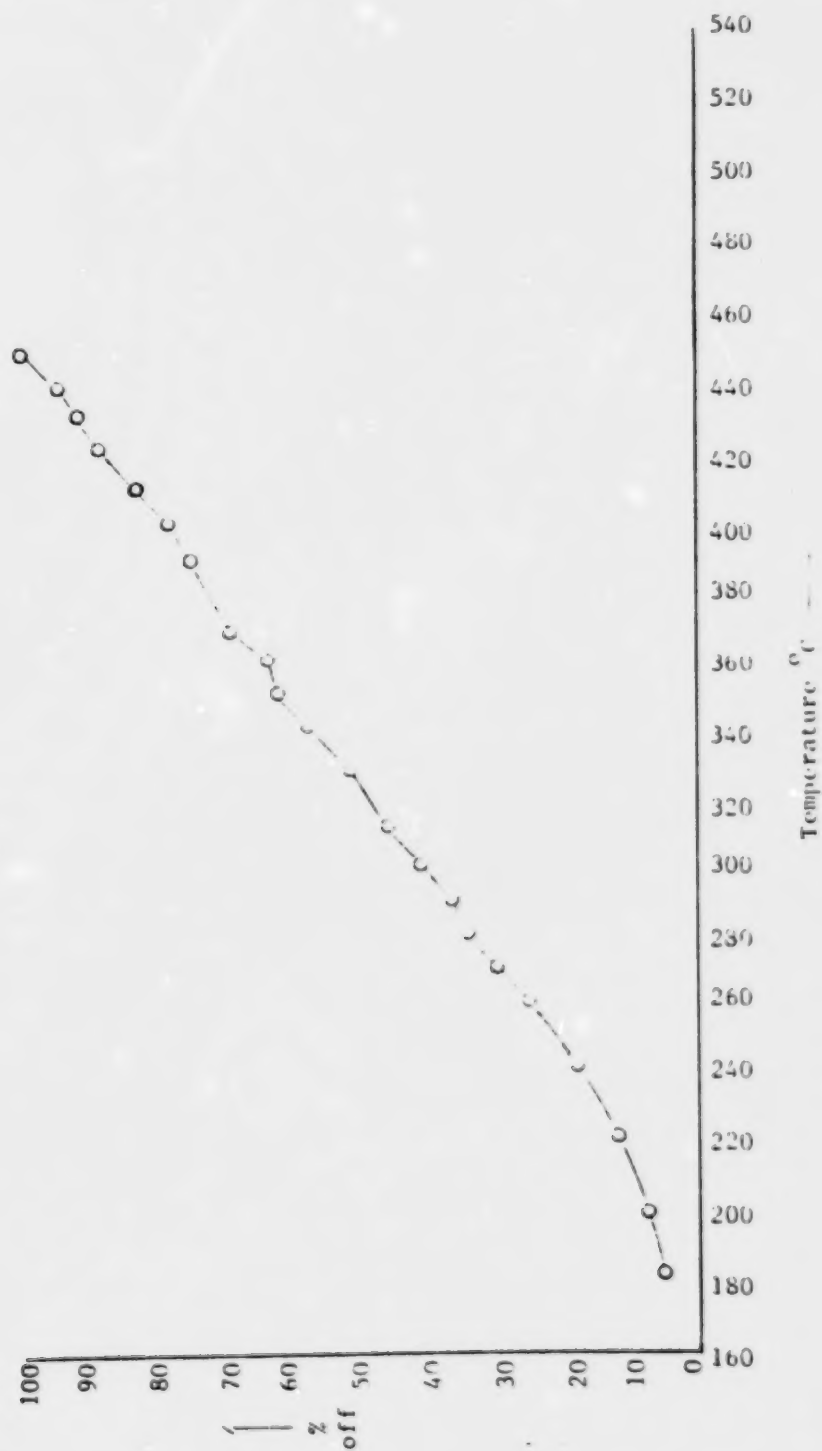


Figure 69
Heavy Liquid
Typical Cumulative % boiling off Vs. Temperature
Catalyst SnCl_4
Run # pitch Sn01



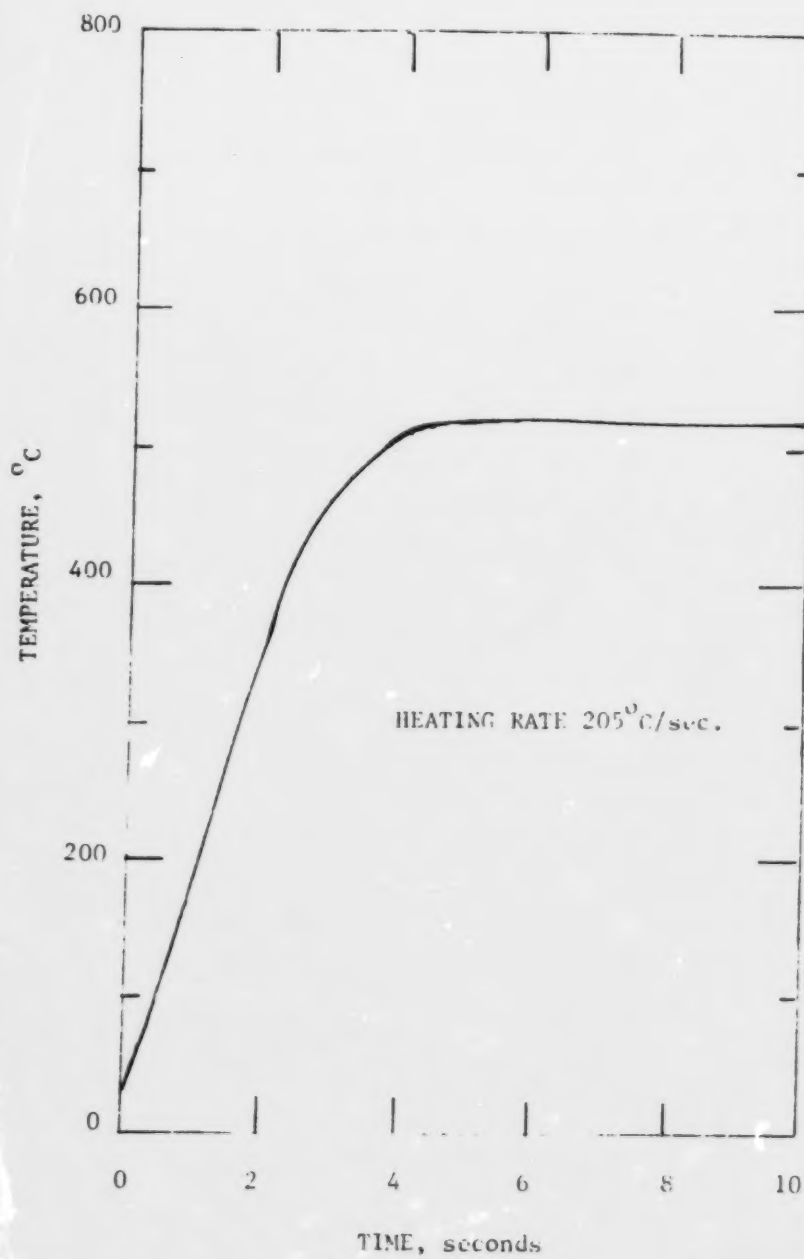


FIGURE 70: Reactor temperature versus time curve. Run No. Pitch Sn 02

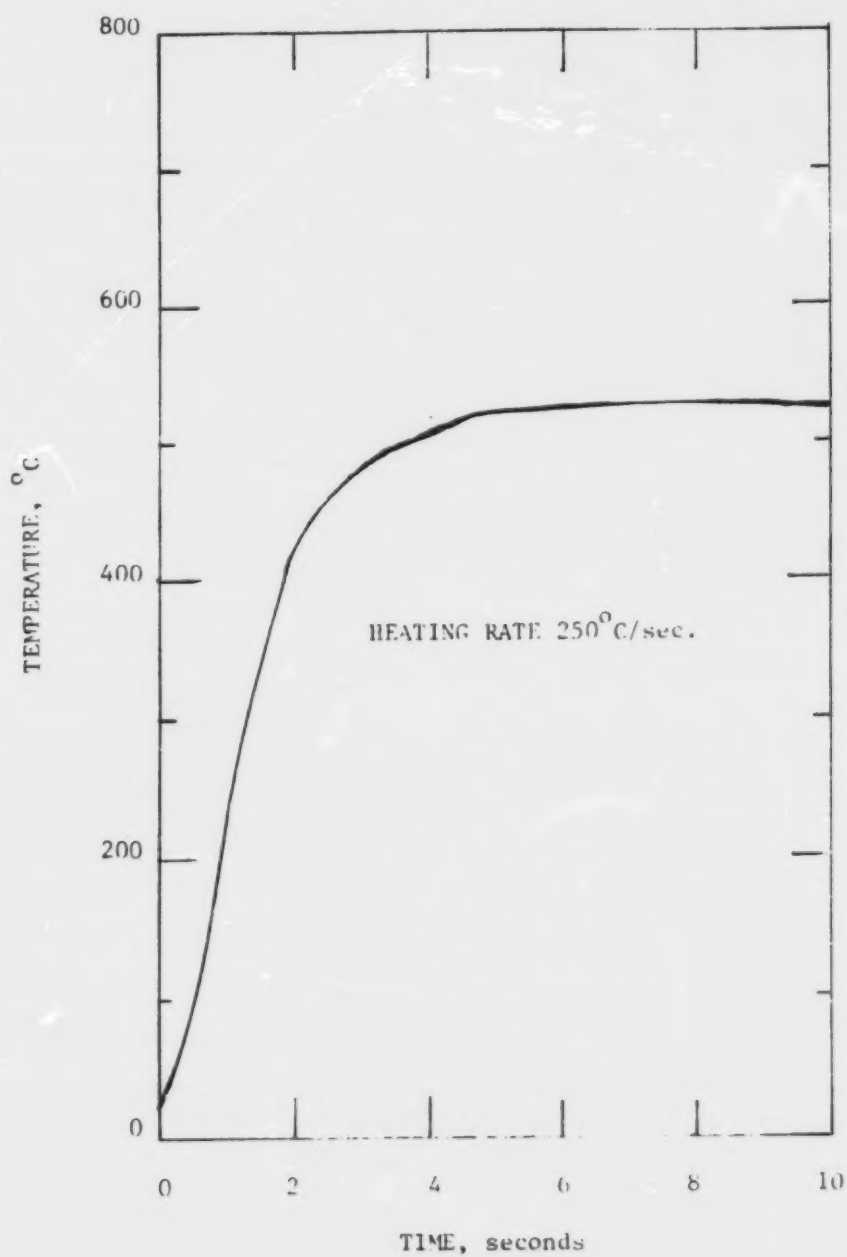


FIGURE 71: Reactor temperature versus time curve. Run No. Pitch Sn 01.

V.4 Results of $\text{ZnO-CrO}_{2/3}$
Catalyzed Experiments

Table 25 : Summary of Run Conditions and
Grouped Product Yields

Run #	pitch ZCD ₁
Catalyst/pitch ratio m/m =	0.315
Maximum Temperature oC =	500
Heating Rate oC sec. =	237
H2 pressure psi =	1,000
residence time sec. =	3:45
mass pitch mg =	57
mass pitch mg C =	46.9
mass catalyst mg total =	18

Product	% of total C
methane	29.5
ethane	24.1
ethene	1.9
propane	3.1
propene	1.8
butane	0.5
butene	0.2
pentane	-
pentene	-
other	-
BTX liquid (light)	18.4
liquid (heavy)	20.0
* Char (residue)	13.0

* Char is whatever is left in the boat after the flash.

Table 26: Summary of Run Conditions and
Grouped Product Yields

	Run #	pitch ZCO ₂
Catalyst/pitch ratio m/m =		0.418
Maximum Temperature oC =		653
Heating Rate oC sec. =		261
H2 pressure psi =		1,000
residence time sec. =		3.95
mass pitch mg =		55
mass pitch mg C =		45.2
mass catalyst mg total =		23

Product	% of total C
methane	37.9
ethane	18.6
ethene	0.9
propane	0.9
propene	0.2
butane	---
butene	-
pentane	-
pentene	-
other	-
BTX liquid (light)	7.65
liquid (heavy)	17.0
* Char (residue)	21.0

* Char is whatever is left in the boat after the flash.

Table AZC03: Summary of Run Conditions and Grouped Product Yields

Run # pitch ZC03

Catalyst/pitch ratio m/m = 0.460

Maximum Temperature $^{\circ}$ C = 500

Heating Rate $^{\circ}$ C /sec = 118

H Pressure psi = 1000

² residence time sec = 3.95

mass pitch mg = 46.0

mass pitch mg C = 37.9

mass catalyst mg total = 21.0

Product	% of total C
C	12.3
1	
C	11.1
2	
C	3.2
3	
C	0.3
4	
C	---
5	
other	---
BTX liquid (light)	2.6
Liquid (heavy)	40.2
* Char (residue)	---

* Char is whatever is left in the boat after the flash.

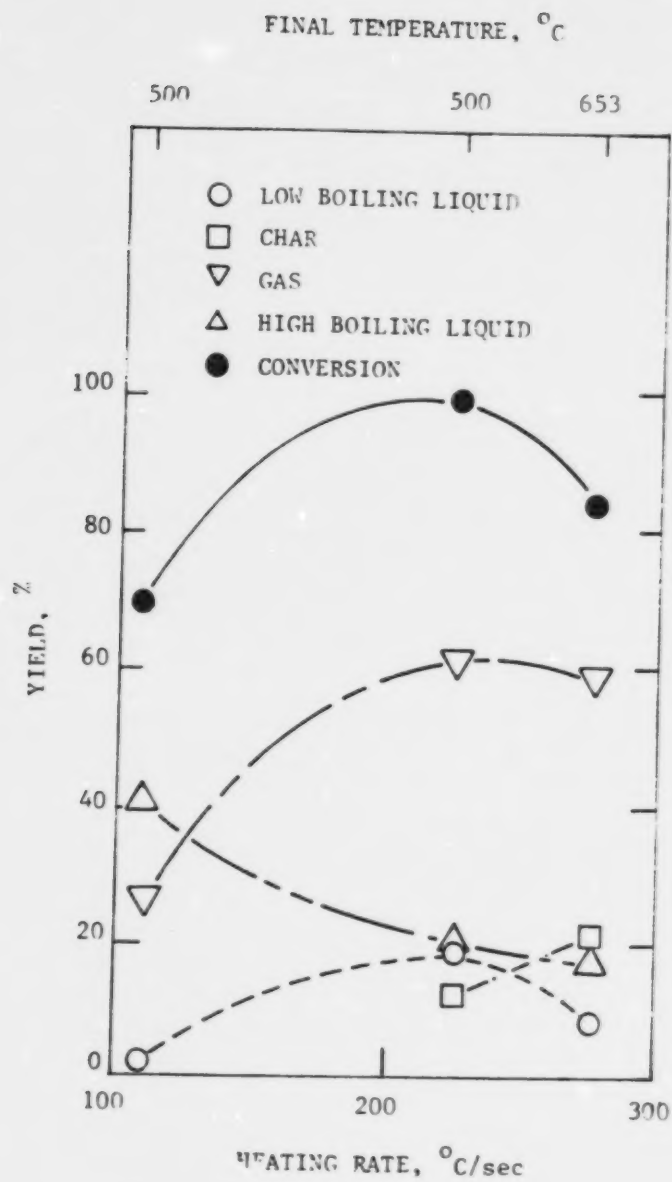
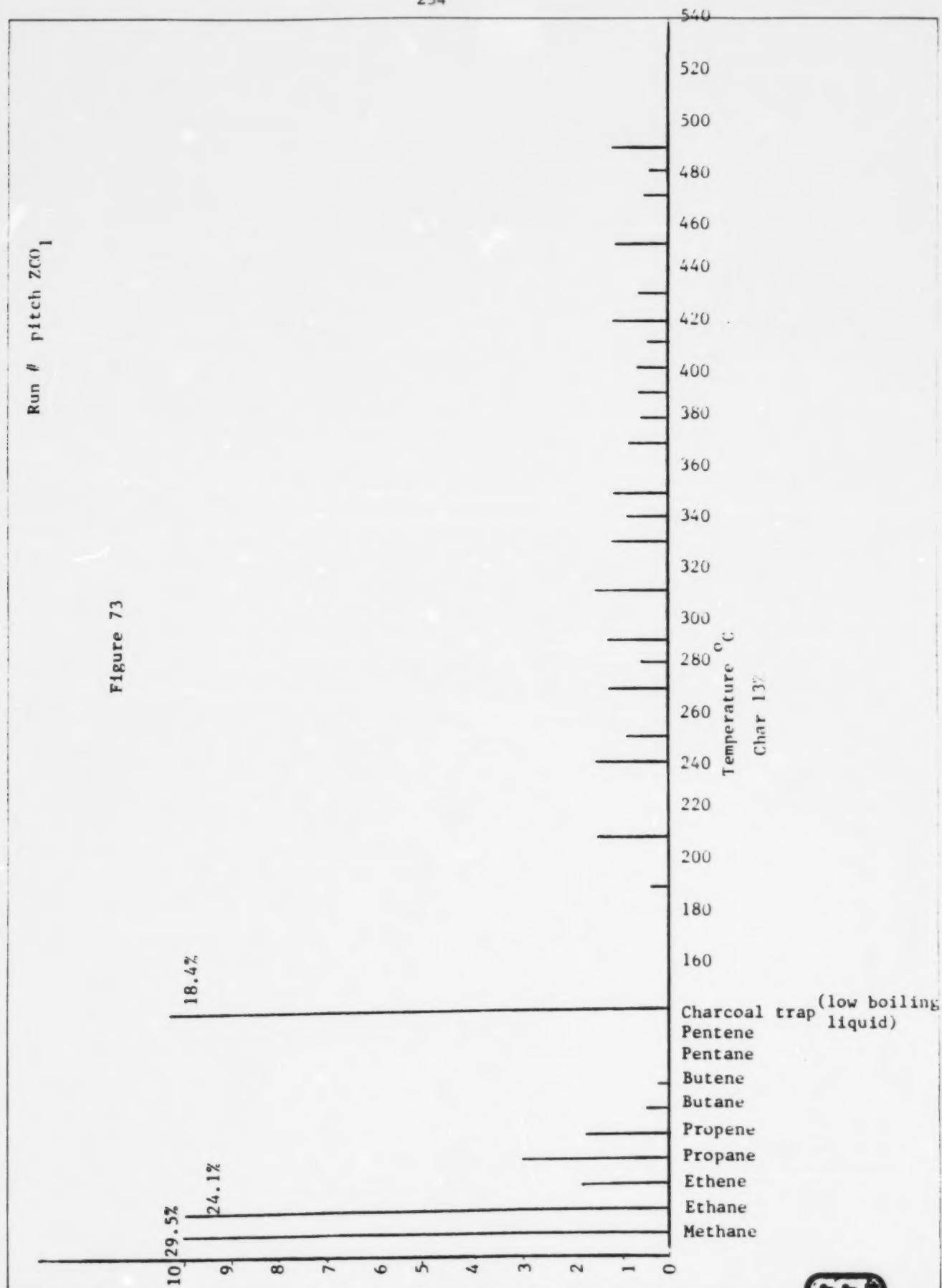


FIGURE 72: Plot of yield versus heating rate. Run No. Pitch ZC01, ZC02, ZC03. System: $\text{ZnO}_2 - \text{Cr}_2\text{O}_7$

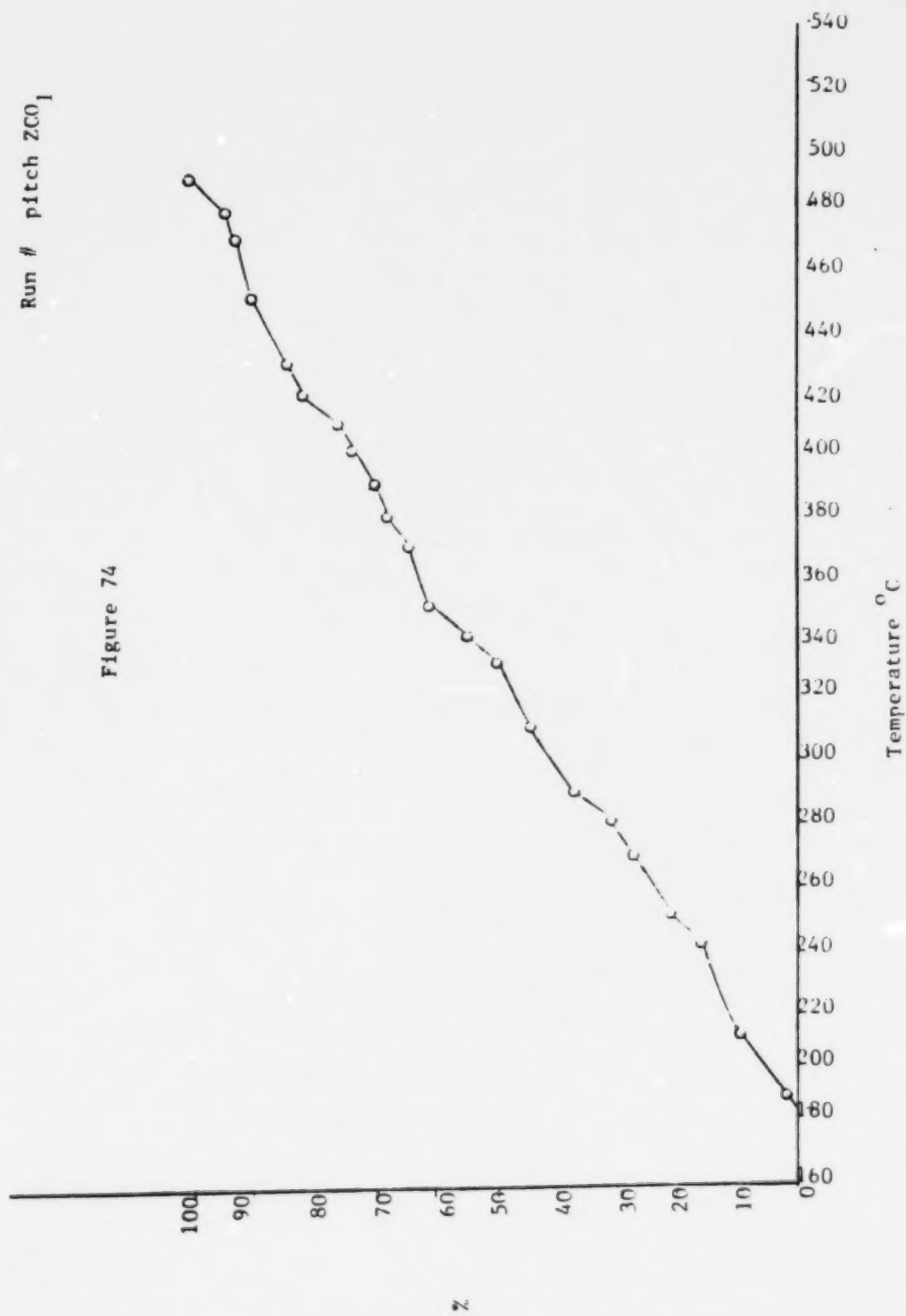
Run # Pitch ZCO₁

Figure 73



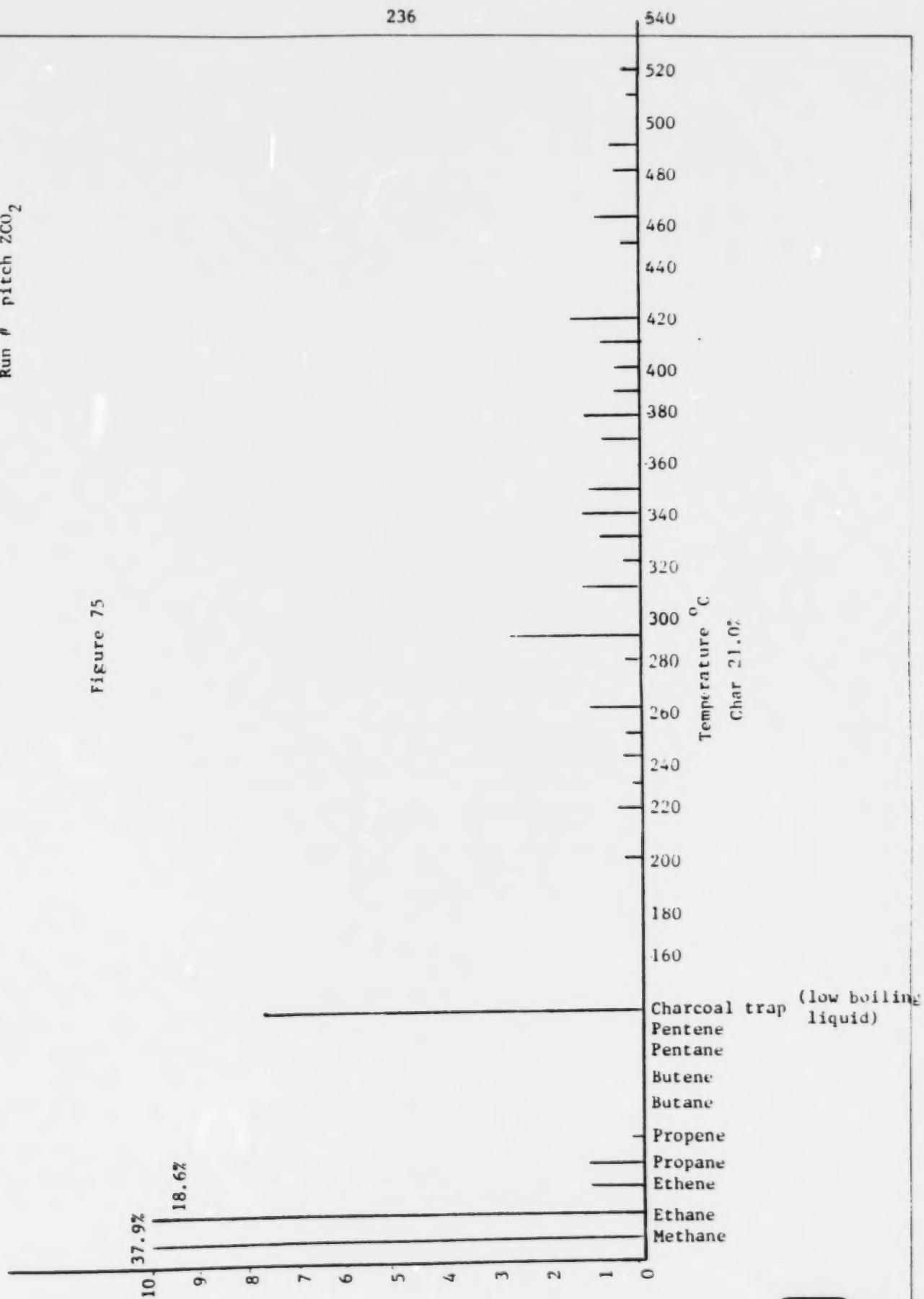
Run # pitch ZCO₁

Figure 74



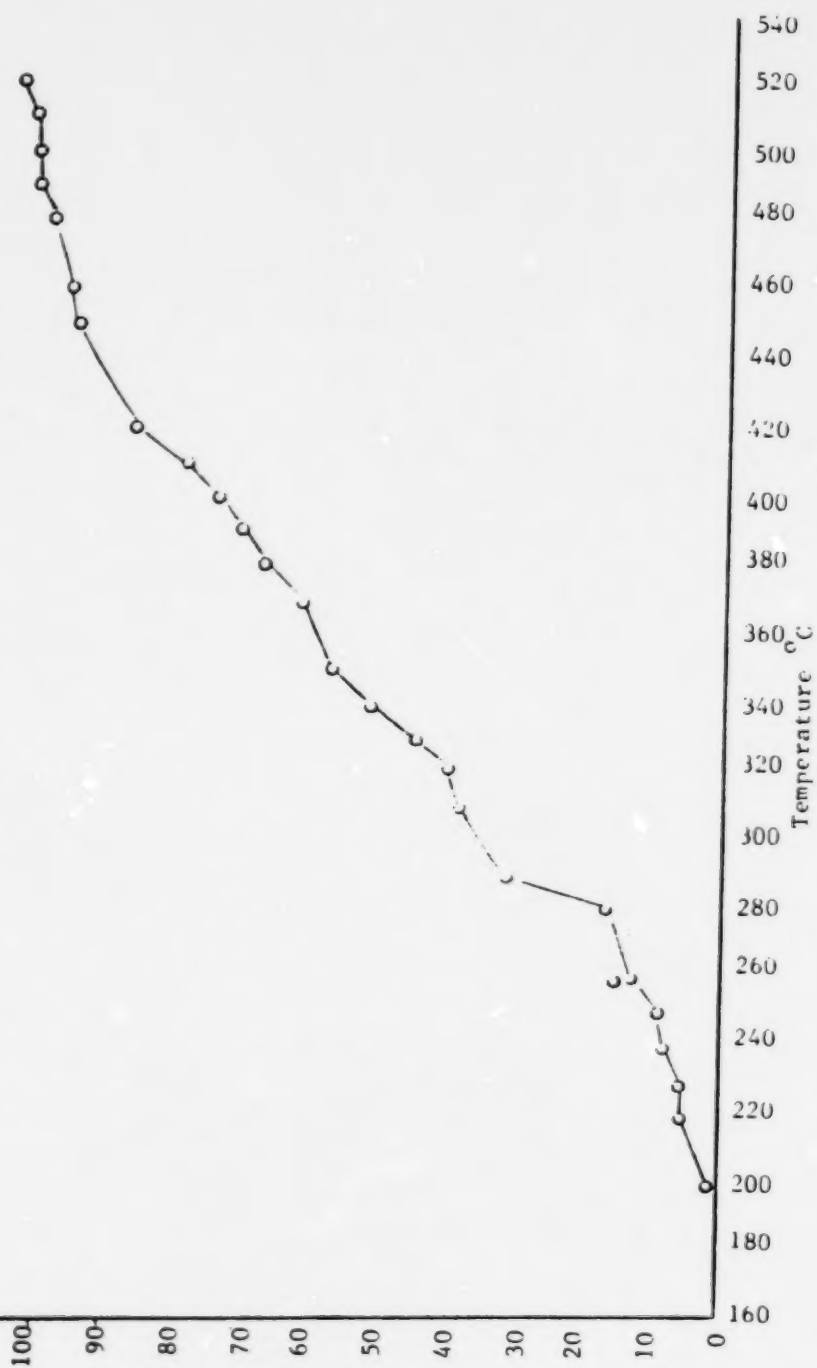
Run # pitch ZCO₂

Figure 75



Run # ZCO₂

Figure 76



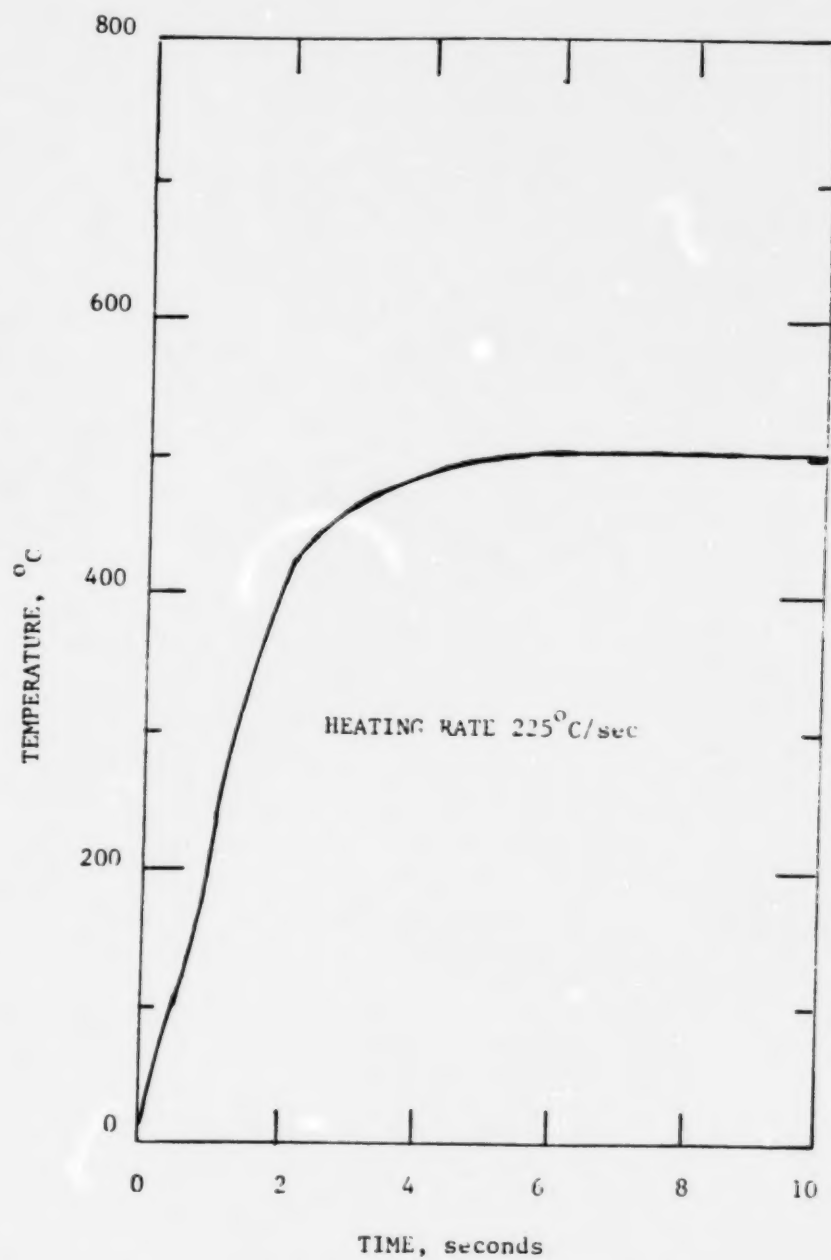


FIGURE 77: Reactor temperature versus time curve. Run No. Pitch ZC 01

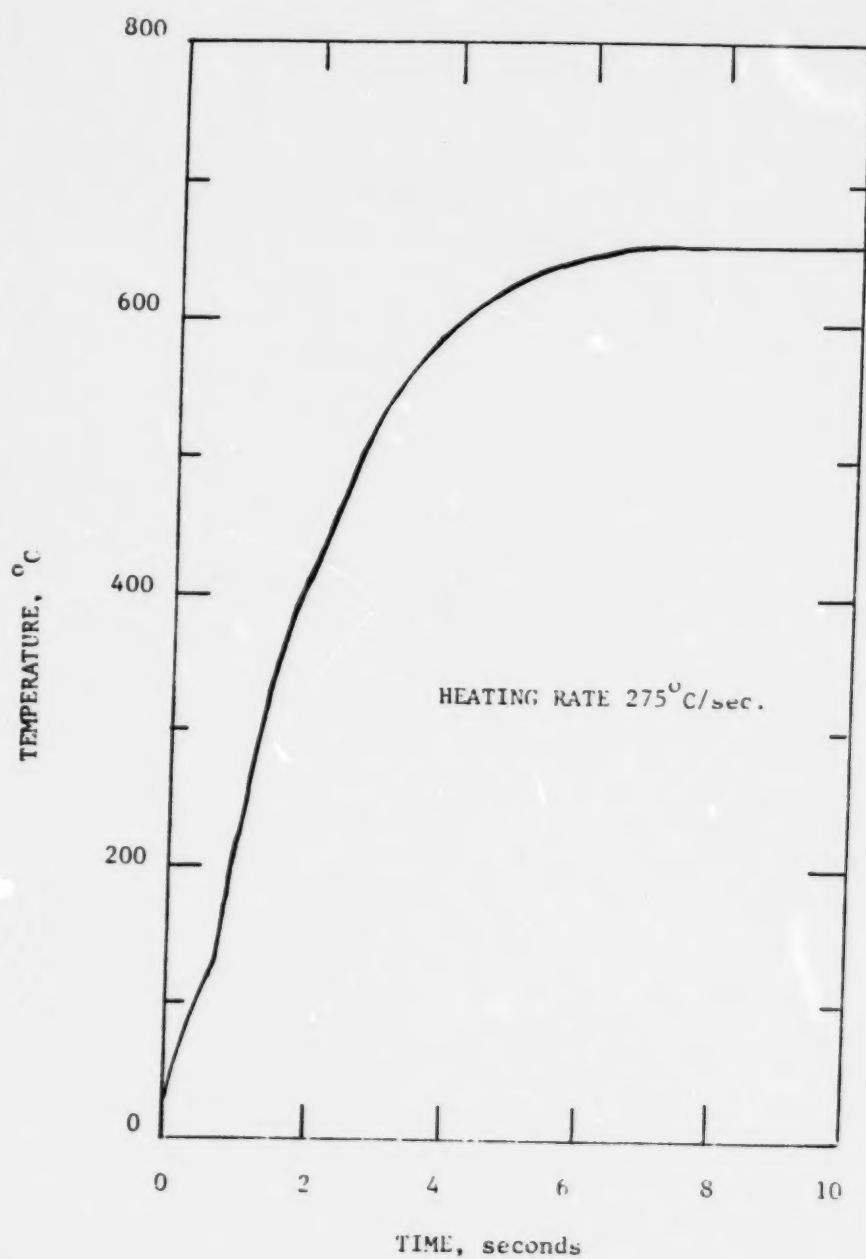


FIGURE 78: Reactor temperature versus time curve. Run No. Pitch ZC 02.

V.5 Results of FeSO_4
Catalyzed Experiments

Table 27

Run #	pitch FS03
Catalyst/pitch ratio m/m	= 0.608
Maximum Temperature oC	= 559
Heating Rate oC sec.	= 237
H2 pressure psi	= 1,000
residence time sec.	= 3.95
mass pitch mg	= 46
mass pitch mg C	= 37.6
mass catalyst mg total	= 28

	% of total C
methane	18.59
ethane	17.55
ethene	1.27
propane	4.68
propene	1.41
butane	0.26
butene	--
pentane	—
pentene	—
other	—
BTX liquid (light)	9.4
liquid (heavy)	26.2
*Char (residue)	24.9

* Char is whatever is left in the boat after the flash

Table 28

Run #	pitch FS05
Catalyst/pitch ratio m/m =	0.518
Maximum Temperature oC =	475
Heating Rate oC sec. =	196
H2 pressure psi =	1,000
residence time sec. =	3.95
mass pitch mg =	54
mass pitch mg C =	44.4
mass catalyst mg total =	28

 % of total C

methane	4.12
ethane	3.51
ethene	1.01
propane	2.86
propene	1.82
butane	0.36
butene	0.76
pentane	0.18
pentene	0.11
other	—
BTX liquid (light)	9.5
liquid (heavy)	40.7
*Char (residue)	25.9

* Char is whatever is left in the boat after the flash
Run taken at low temperature.

Table 29

Run #	pitch FS06
Catalyst/pitch ratio m/m	= 0.818
Maximum Temperature oC	= 458
Heating Rate oC sec.	= 237
H2 pressure psi	= 1,000
residence time sec.	= 3.95
mass pitch mg	= 44
mass pitch mg C	= 36.2
mass catalyst mg total	= 36

	% of total C
methane	12.45
ethane	12.79
ethene	3.25
propane	6.54
propene	3.26
butane	0.94
butene	1.60
pentane	0.22
pentene	-
other	-
BTX liquid (light)	5.3
liquid (heavy)	24.0
*Char (residue)	29.4

* Char is whatever is left in the boat after the flash

Table 30

Run #	pitch FS09
Catalyst/pitch ratio m/m	= 0.777
Maximum Temperature oC	= 488
Heating Rate oC sec.	= 213
H2 pressure psi	= 1,000
residence time sec.	= 3.95
mass pitch mg	= 45
mass pitch mg C	= 37.0
mass catalyst mg total	= 35

	% of total C
methane	2.45
ethane	2.89
ethene	0.97
propane	2.83
propene	2.62
butane	0.46
butene	0.51
pentane	—
pentene	—
other	—
BTX liquid (light)	7.9
liquid (heavy)	39.7
*Char (residue)	32.7

* Char is whatever is left in the boat after the flash

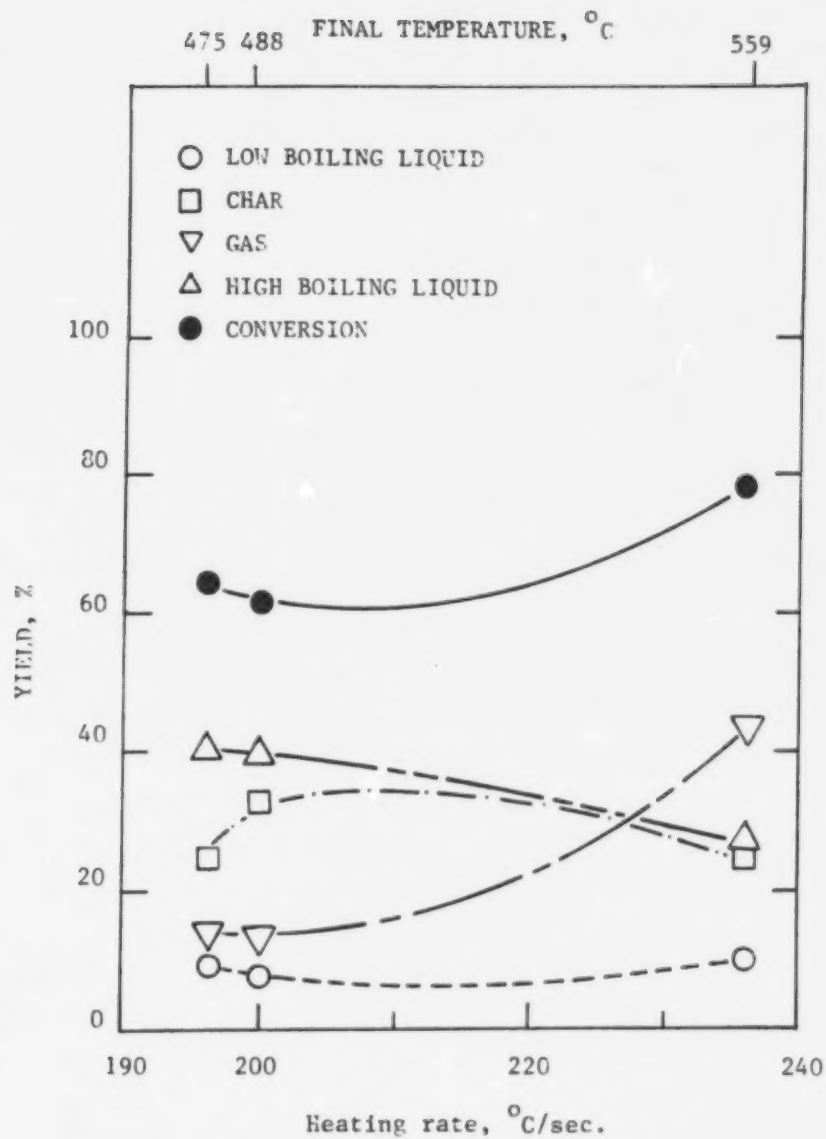


FIGURE 79: A plot of yield versus heating rate.
Run Nos. Pitch FS03, FS05 and FS09. System:
 $\text{Fe}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$.

Table AFS07: Summary of Run Conditions and Grouped Product Yields

Run # pitch FS07

Catalyst/pitch ratio m/m = 0.860

Maximum Temperature $^{\circ}$ C = 500

Heating Rate $^{\circ}$ C /sec = 218

H Pressure psi = 1000

^{2} residence time sec = 3.95

mass pitch mg = 50.0

mass pitch mg C = 41.1

mass catalyst mg total = 43.0

Product	% of total C
C	21.6
1	
C	16.9
2	
C	0.6
3	
C	---
4	
C	---
5	
other	---
BTX liquid (light)	8.1
Liquid (heavy)	17.3
* Char (residue)	17.3

* Char is whatever is left in the boat after the flash.

Table AFS08: Summary of Run Conditions and
Grouped Product Yields

Run # pitch FS08

Catalyst/pitch ratio m/m = 0.698

Maximum Temperature $^{\circ}\text{C}$ = ---

Heating Rate $^{\circ}\text{C} / \text{sec}$ = ---

H Pressure psi = 1000

^{2} residence time sec = 3.95

mass pitch mg = 43.0

mass pitch mg C = 35.4

mass catalyst mg total = 30.0

Product	% of total C
C	18.4
1	
C	18.2
2	
C	2.1
3	
C	---
4	
C	---
5	
other	---
BTX liquid (light)	---
Liquid (heavy)	16.5
* Char (residue)	25.0

* Char is whatever is left in the boat after the flash.

Figure 80

Heavy Liquid
Typical Cumulative % boiling off Vs. Temperature
Catalyst $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
Run # pitch FS03

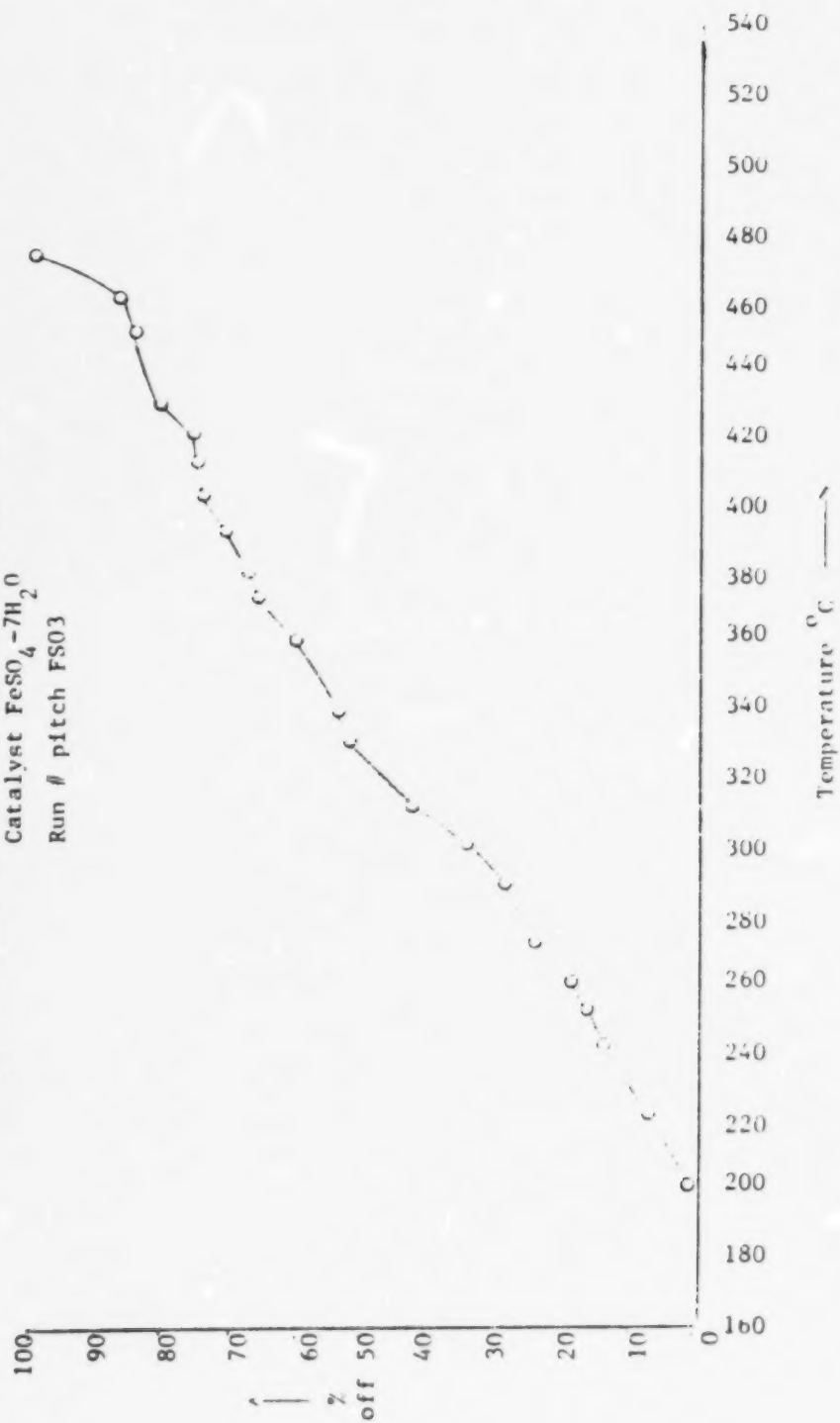
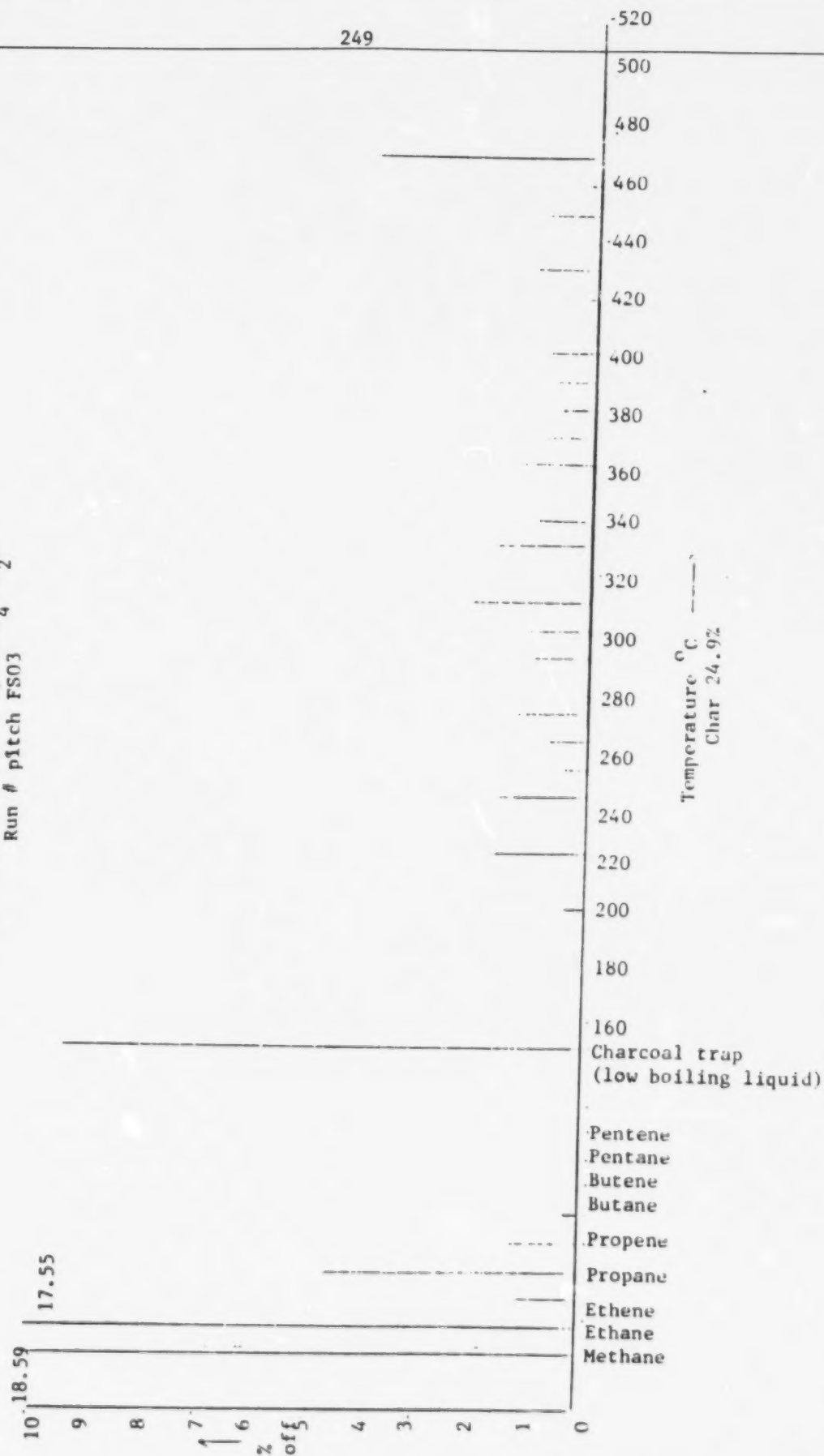


Figure 81
Histogram of % Boiling Distribution
of Pitch Catalyzed by $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
Run # pitch FS03



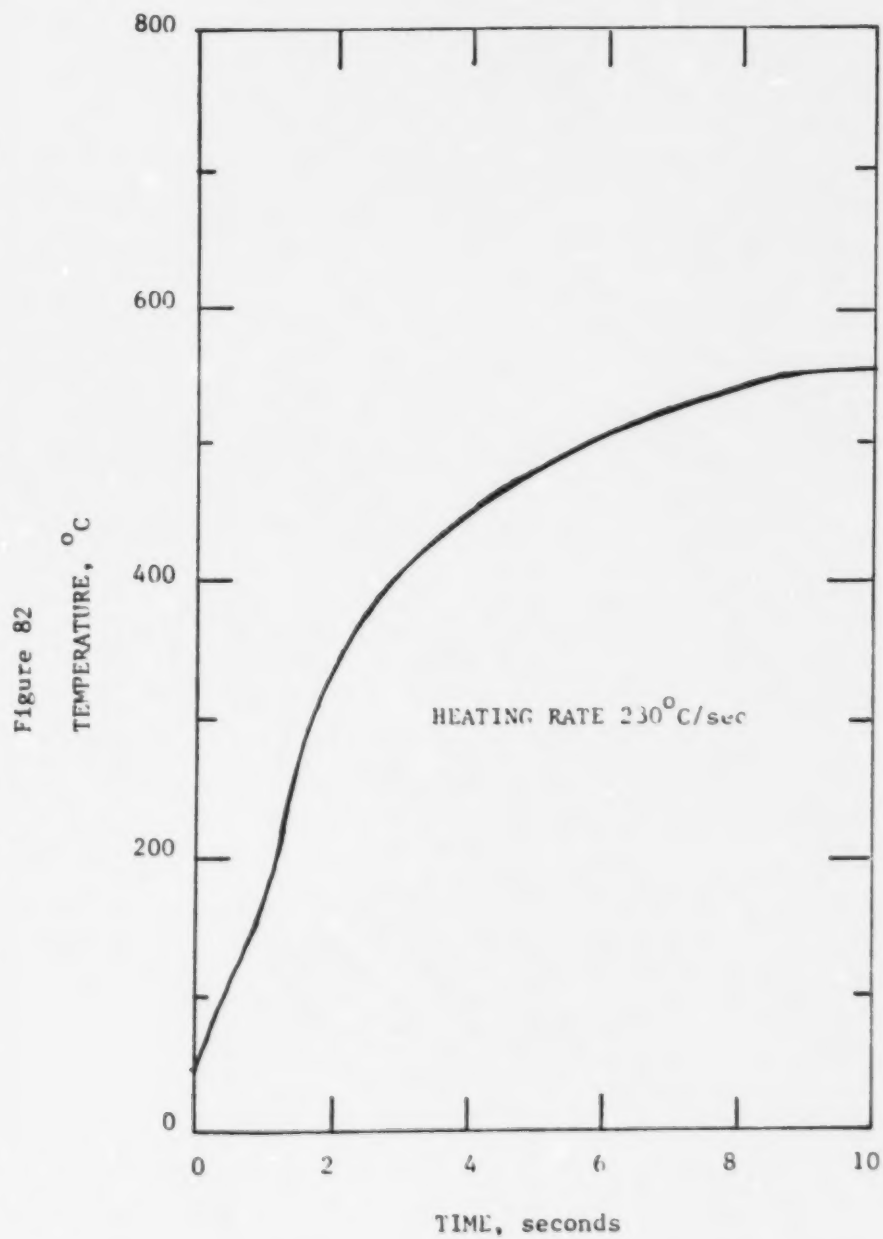


FIGURE: Reactor temperature versus time curve. Run No. Pitch FS 03

Figure 83
Heavy Liquid
Typical Cumulative % boiling off Vs. Temperature
Catalyst $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ run # pitch FSO_5
Run # pitch FSO_5

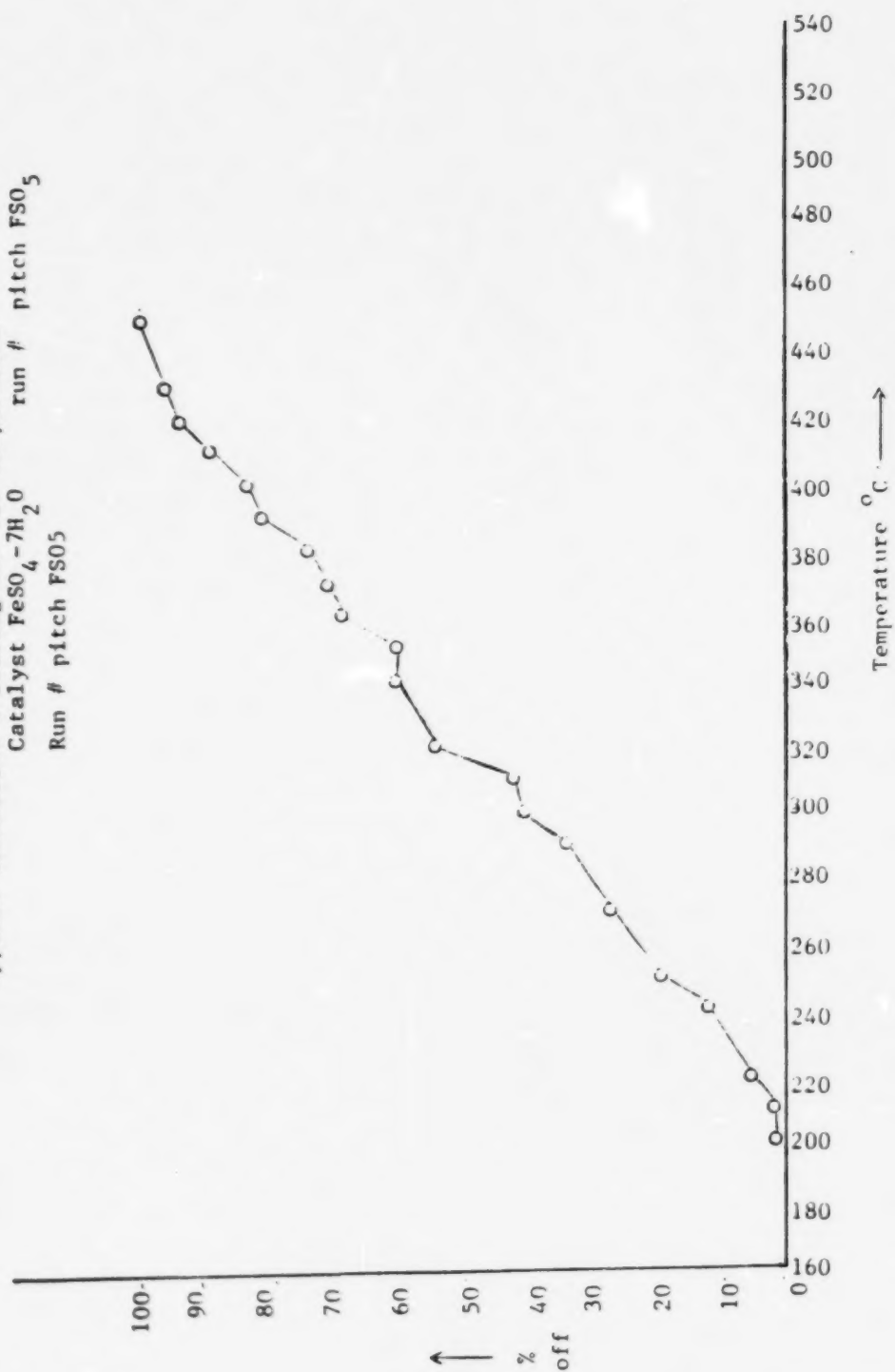


Figure 84

Histogram of % Boiling Distribution
of Pitch Catalyzed by $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$

Run # pitch FS05

run # pitch FS05

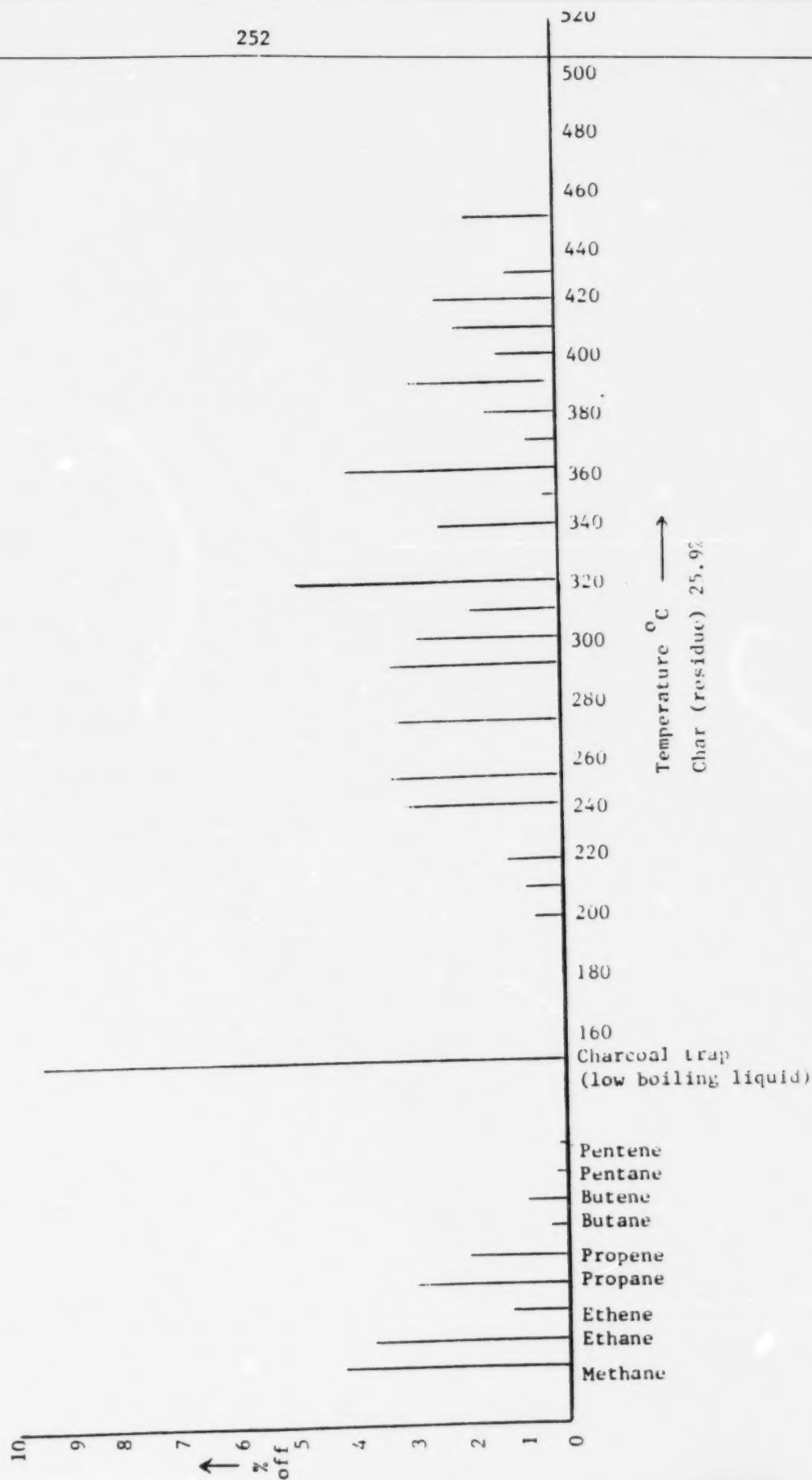


Figure 85
run # pitch FSO₆

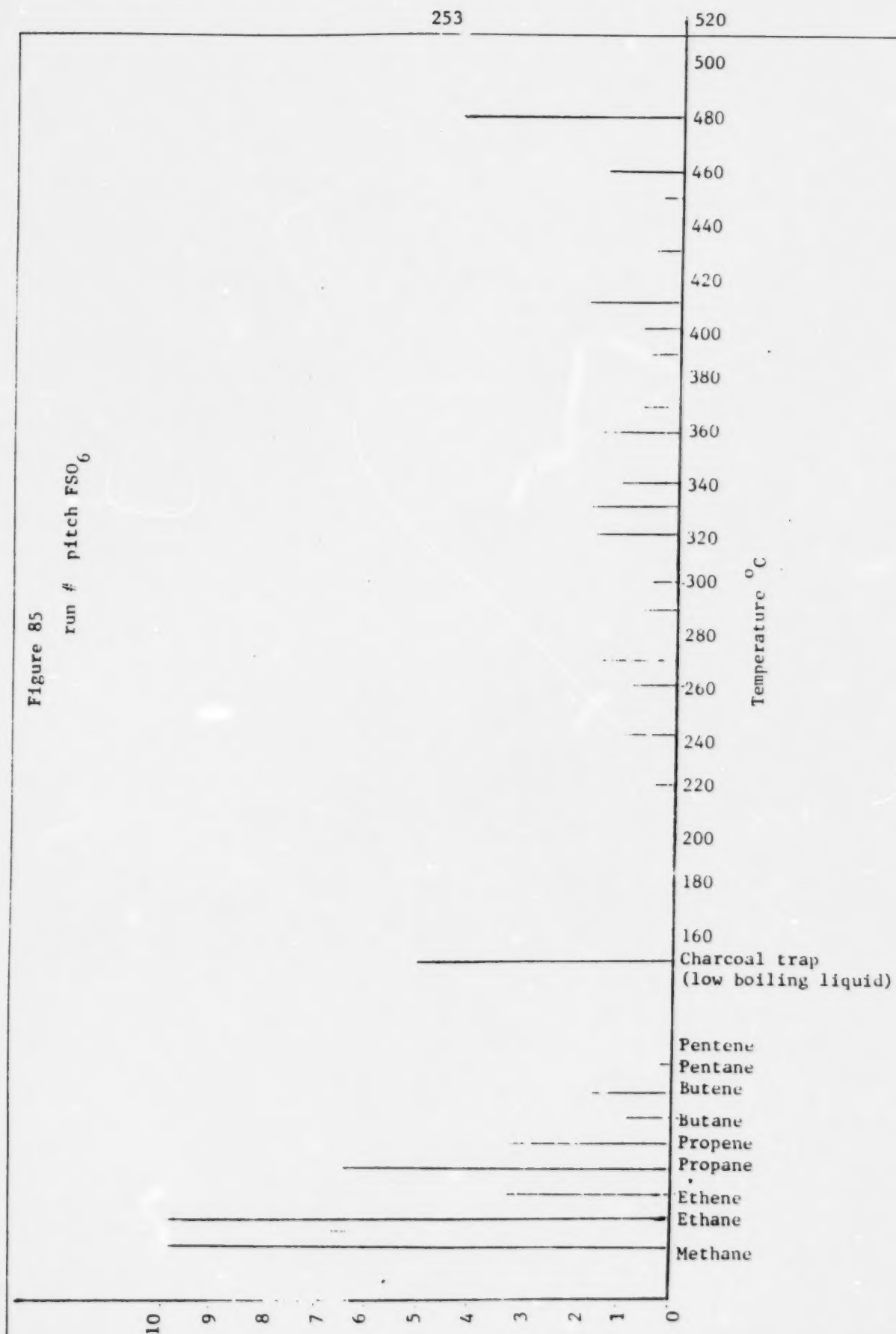


Figure 86

run # FS06

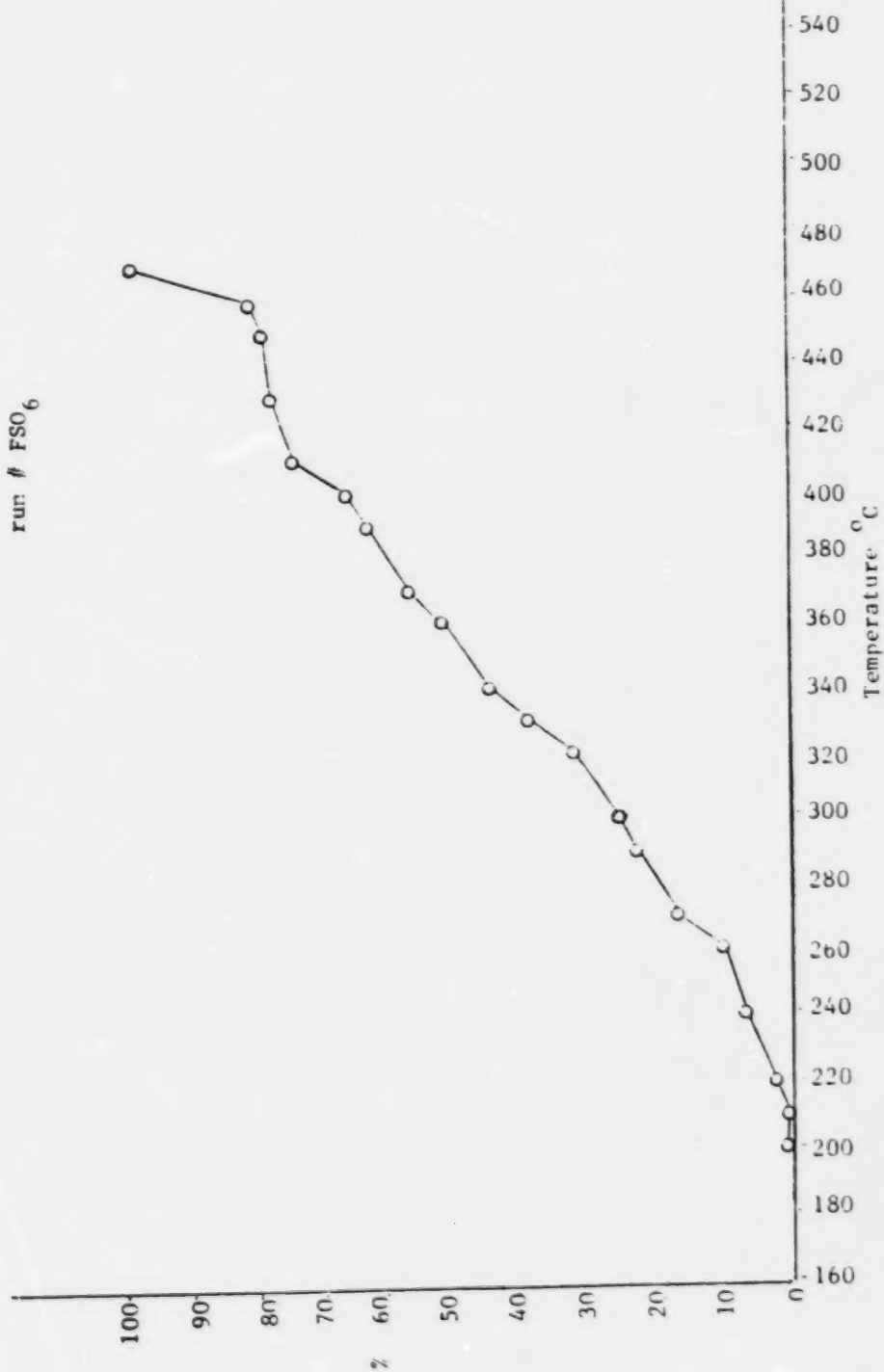


Figure 87

Heavy Liquid
Typical Cumulative % boiling off Vs. Temperature
Catalyst $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
Run # pitch FS09

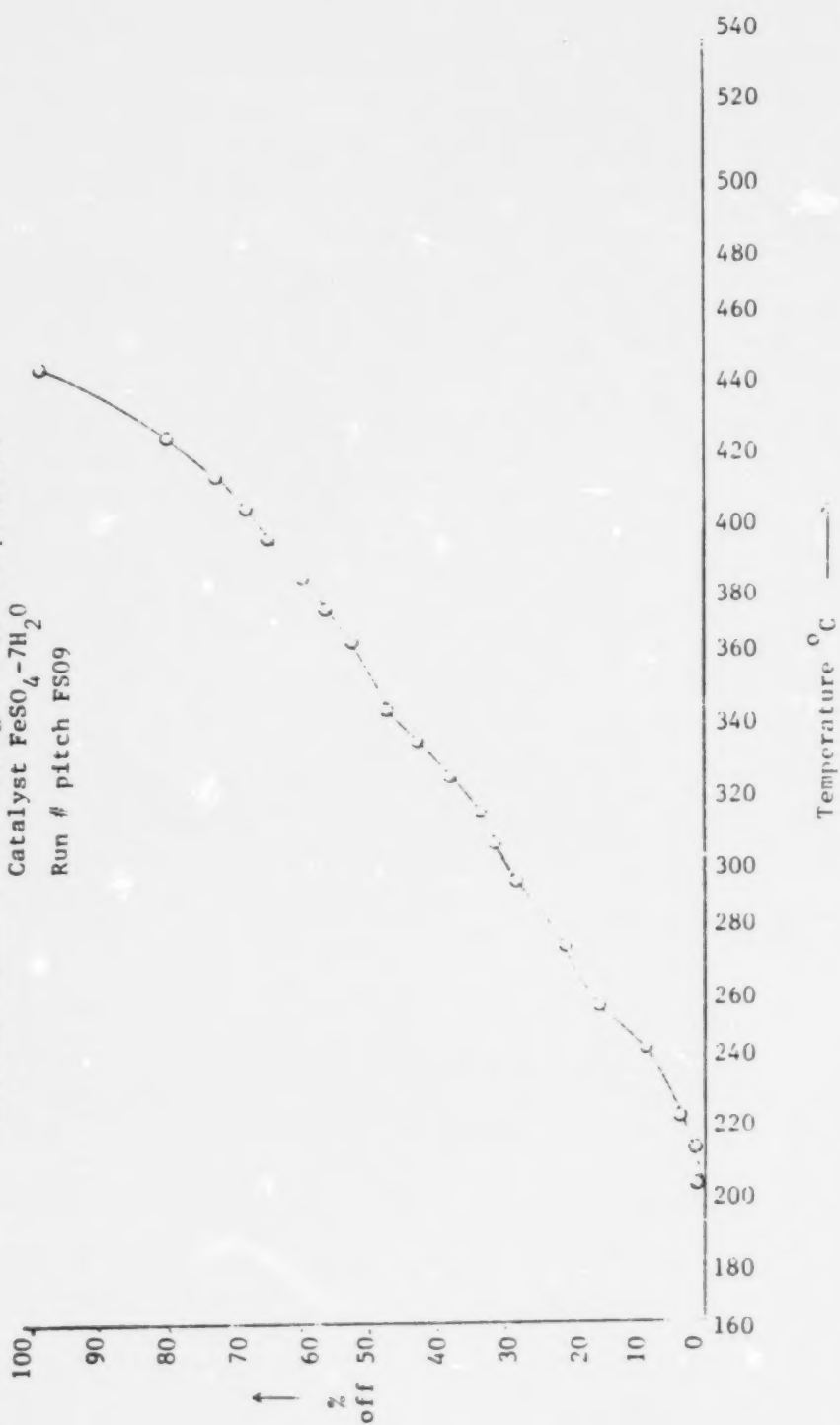
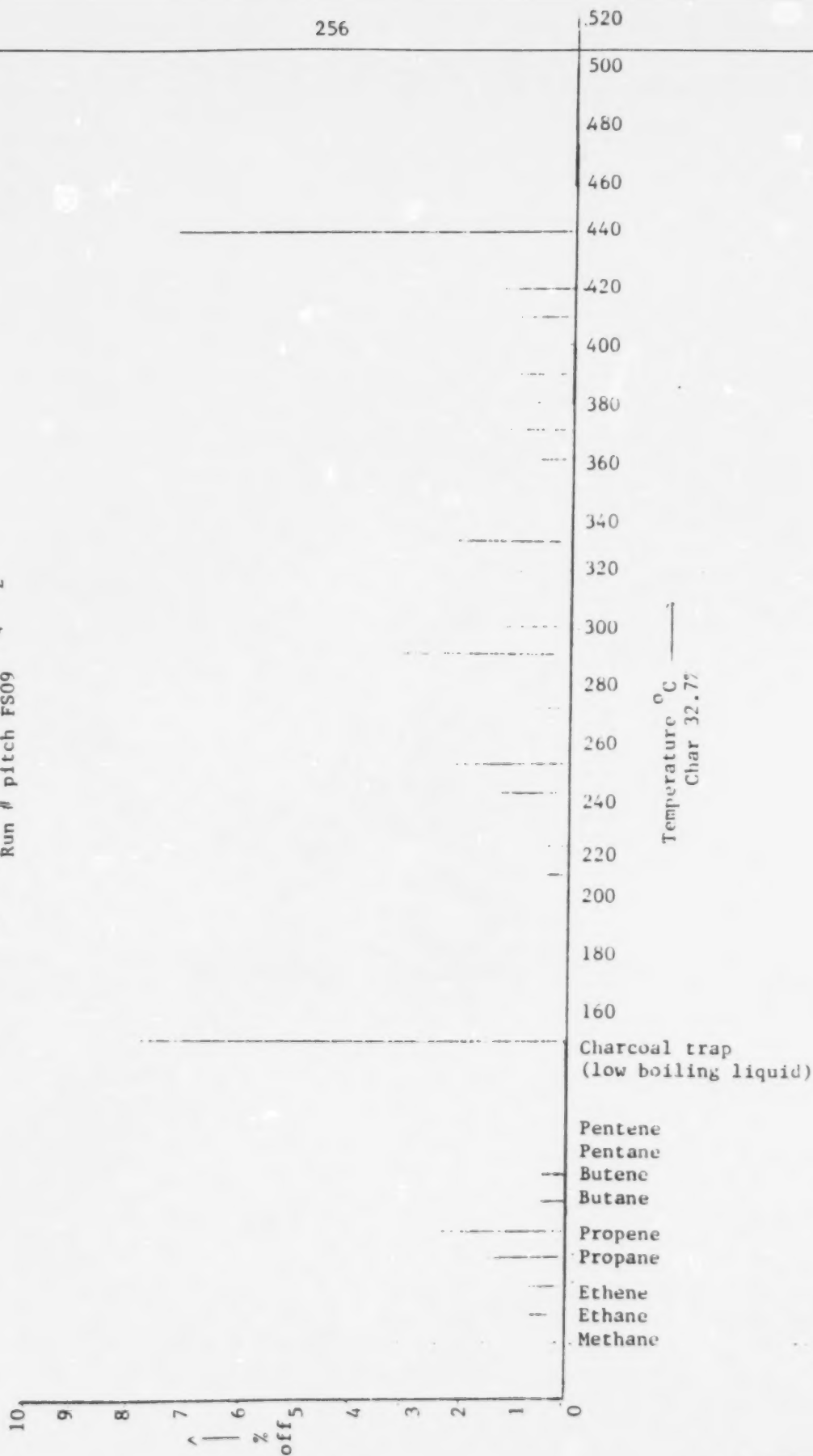


Figure 88
Histogram of % Boiling Distribution
of Pitch Catalyzed by $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
Run # pitch FS09



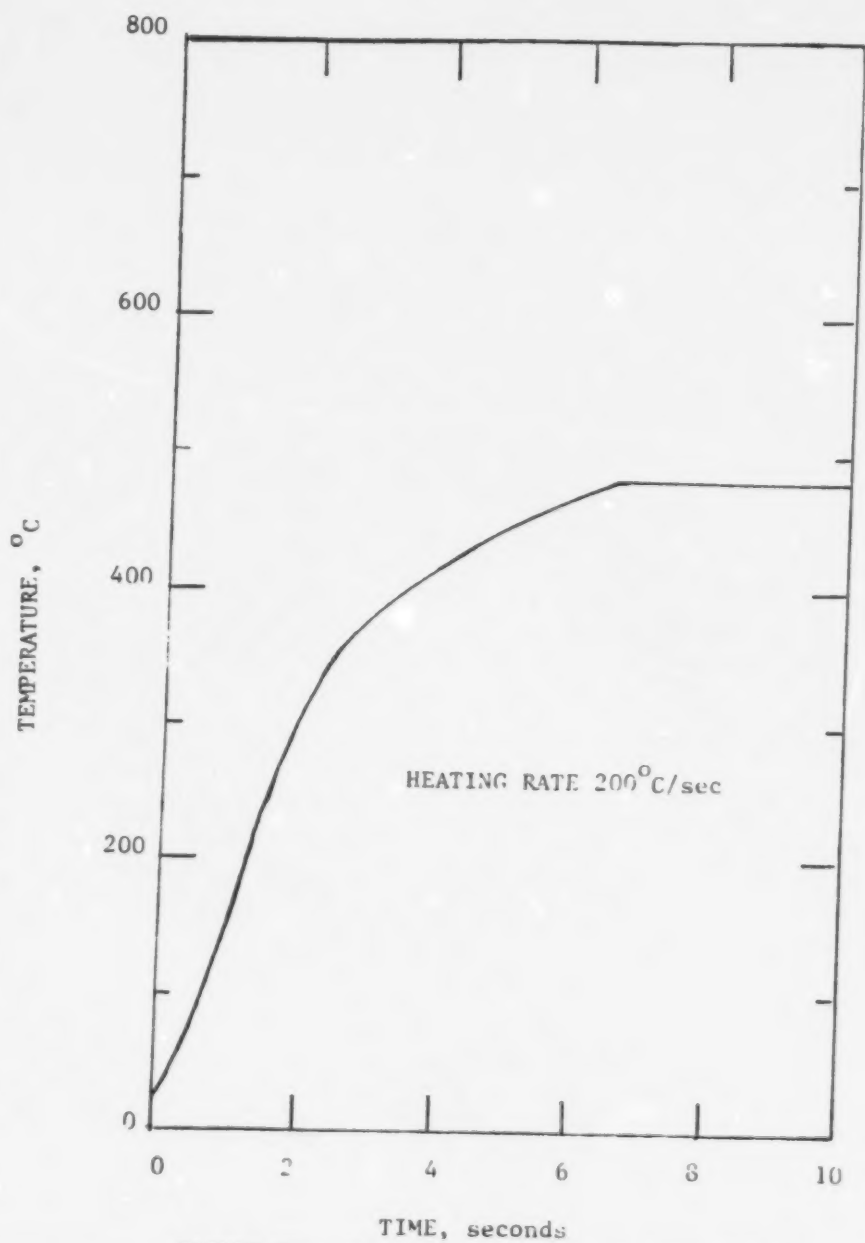


FIGURE 89: Reactor temperature versus time curve. Run No. Pitch FS09

V.6 Results of Mg-SiO₂
Catalyzed Experiments

Table 31: Summary of Run Conditions and
Grouped Product Yields

Run #	pitch M_{O_1}
Catalyst/pitch ratio m/m =	0.384
Maximum Temperature oC =	558
Heating Rate oC sec. =	175
H2 pressure psi =	1,000
residence time sec. =	
mass pitch mg =	52
mass pitch mg C =	42.7
mass catalyst mg total =	20

Product	% of total C
methane	18.1
ethane	19.7
ethene	—
propane	11.9
propene	4.2
butane	1.9
butene	1.1
pentane	1.9
pentene	0.2
other	—
BTX liquid (light)	15.9
liquid (heavy)	17.9
* Char (residue)	18.7

* Char is whatever is left in the boat after the flash.

Table 32: Summary of Run Conditions and Grouped Product Yields

	Run #	pitch M_{gO_2}
Catalyst/pitch ratio m/m =		0.388
Maximum Temperature oC =		594
Heating Rate oC sec. =		270
H2 pressure psi =		1,000
residence time sec. =		
mass pitch mg =		67
mass pitch mg C =		55.1
mass catalyst mg total =		26

Product	% of total C
methane	26.9
ethane	24.3
ethene	1.3
propane	5.0
propene	7.1
butane	0.7
butene	0.3
pentane	—
pentene	—
other	—
BTX liquid (light)	20.0
liquid (heavy)	15.7
* Char (residue)	14.2

* Char is whatever is left in the boat after the flash.

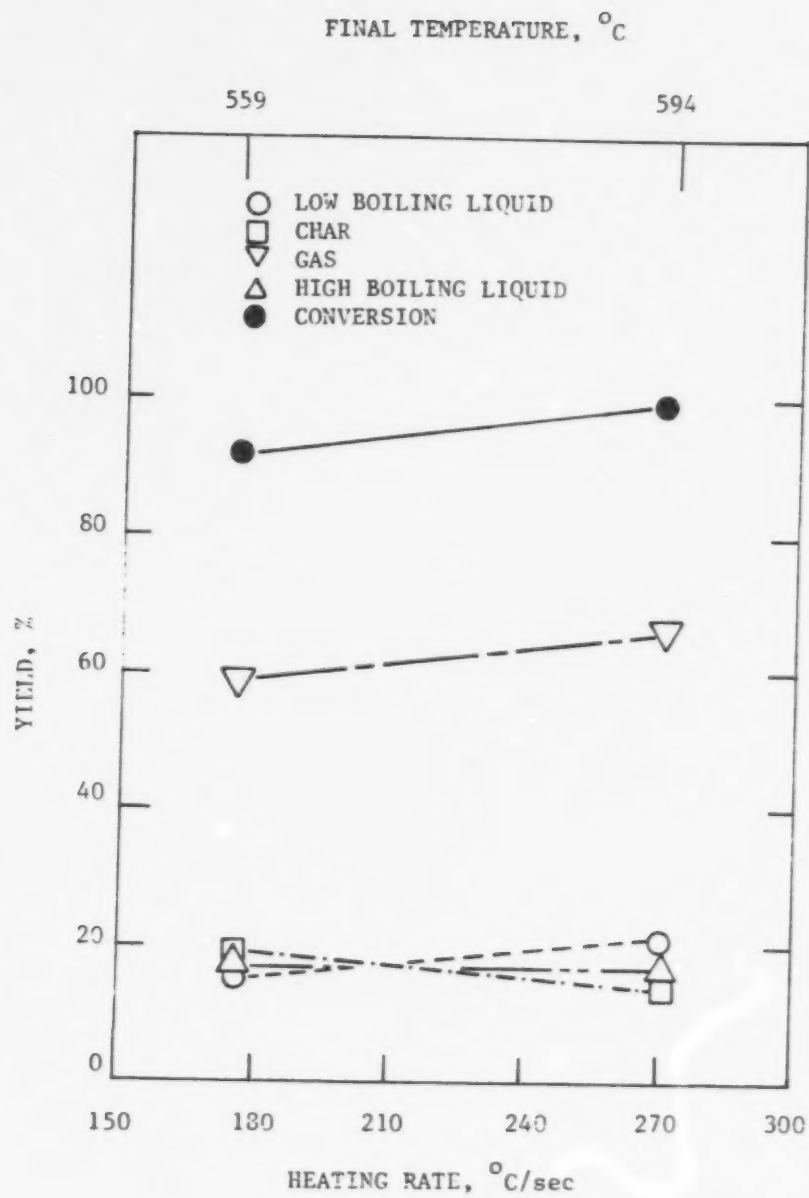
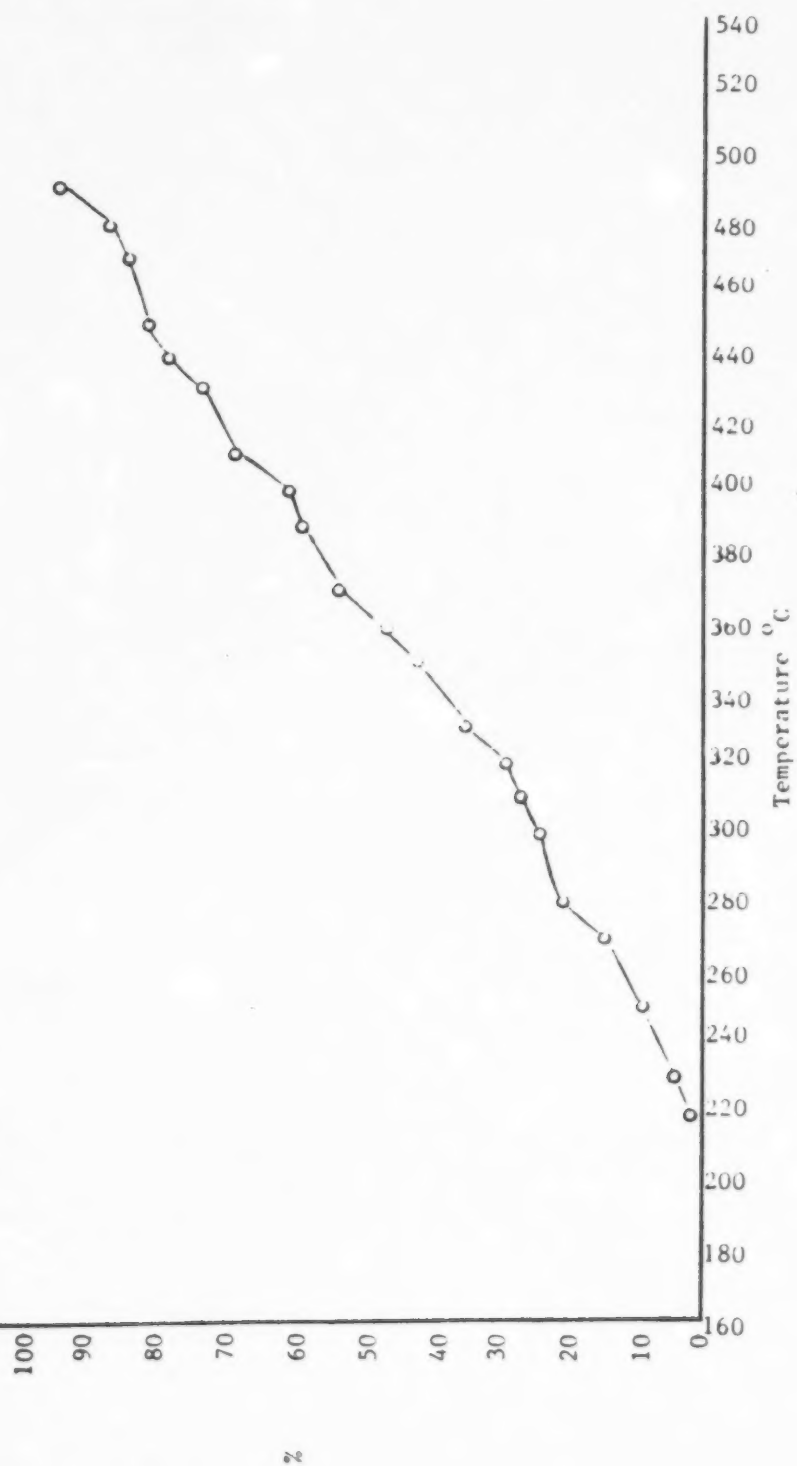


FIGURE 90: A plot of yield versus heating rate.
Run Nos. Pitch Mg01, Ng02, System: MgO - SiO₂.

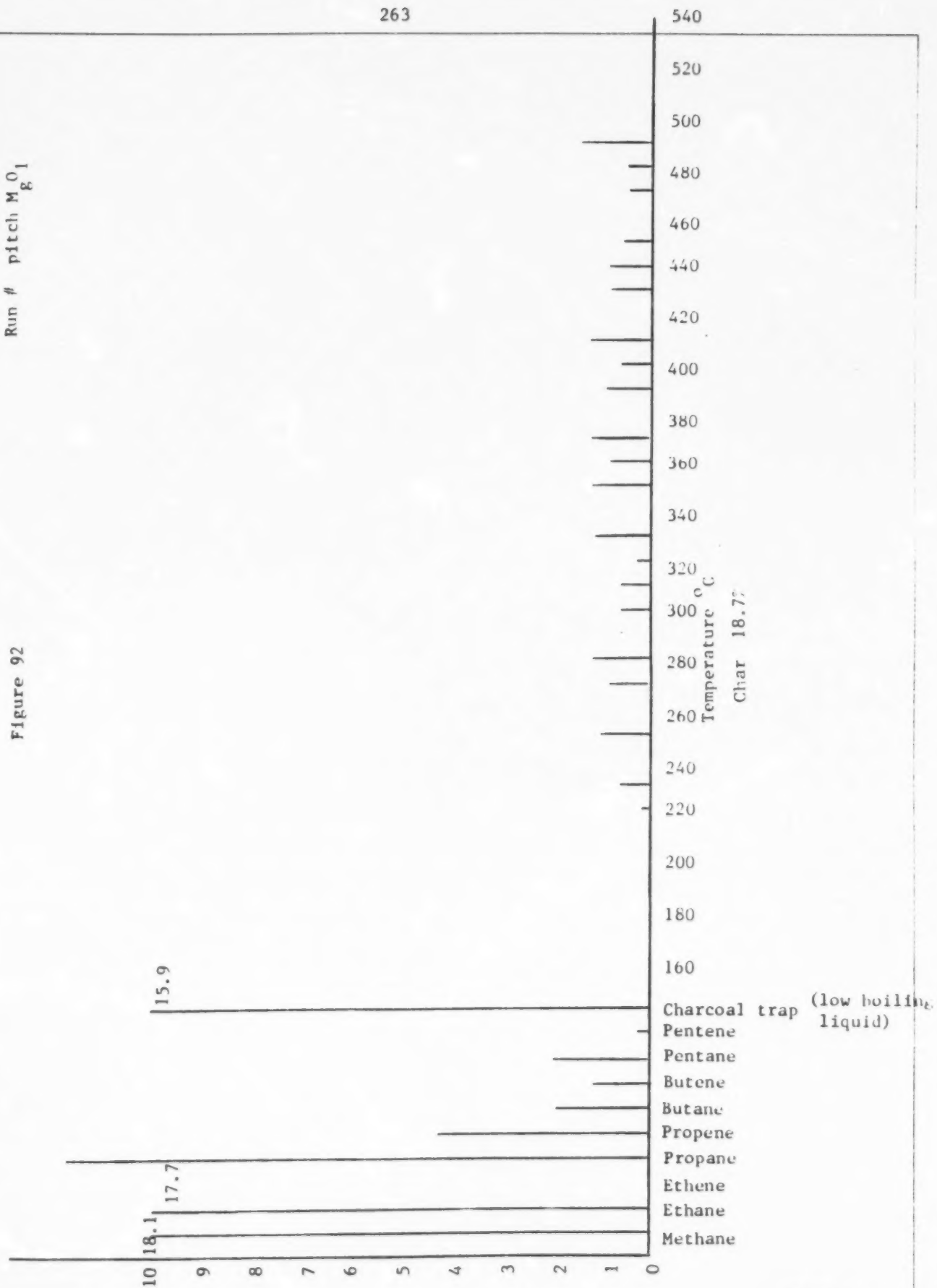
Run # M_gO₁

Figure 91



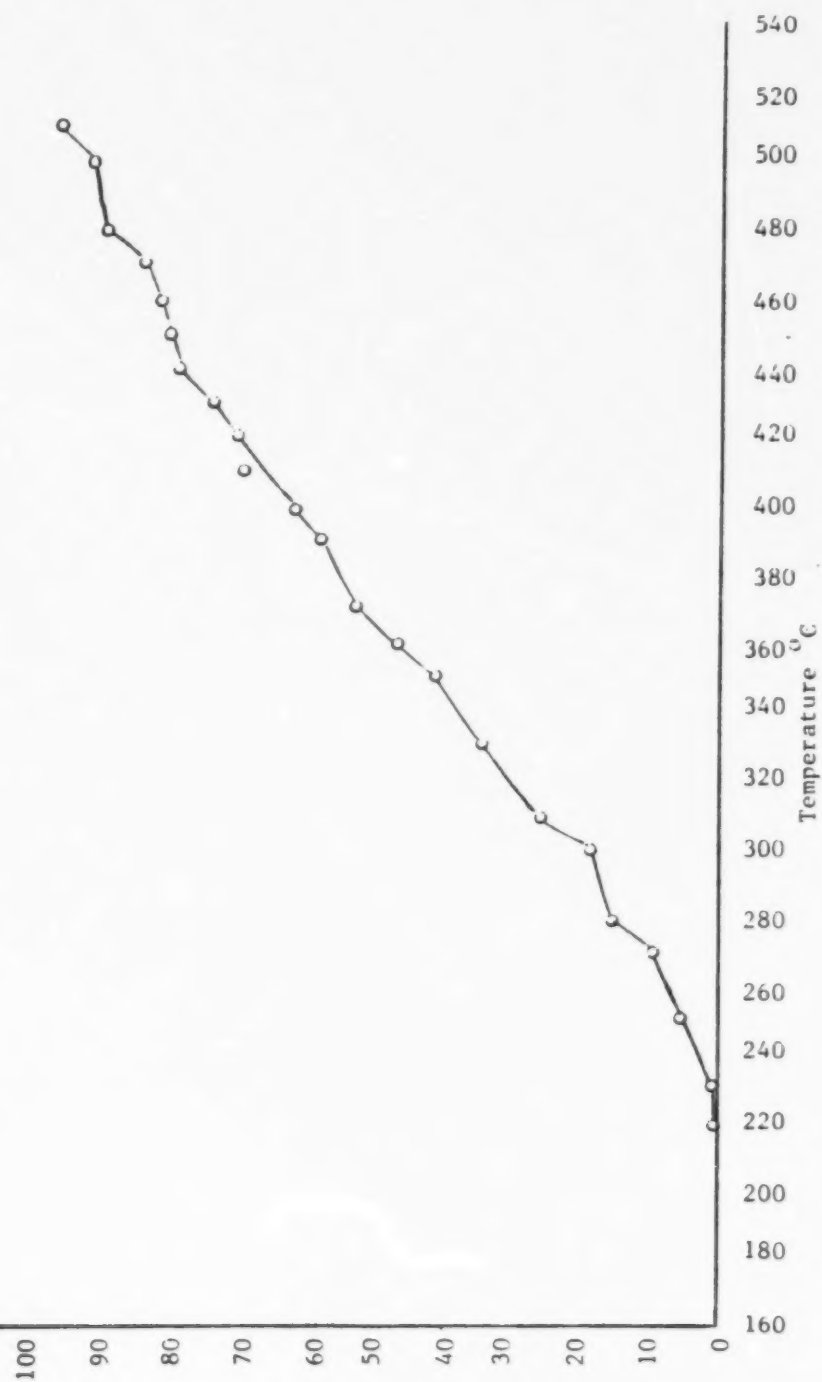
Run # pitch M₀ 1

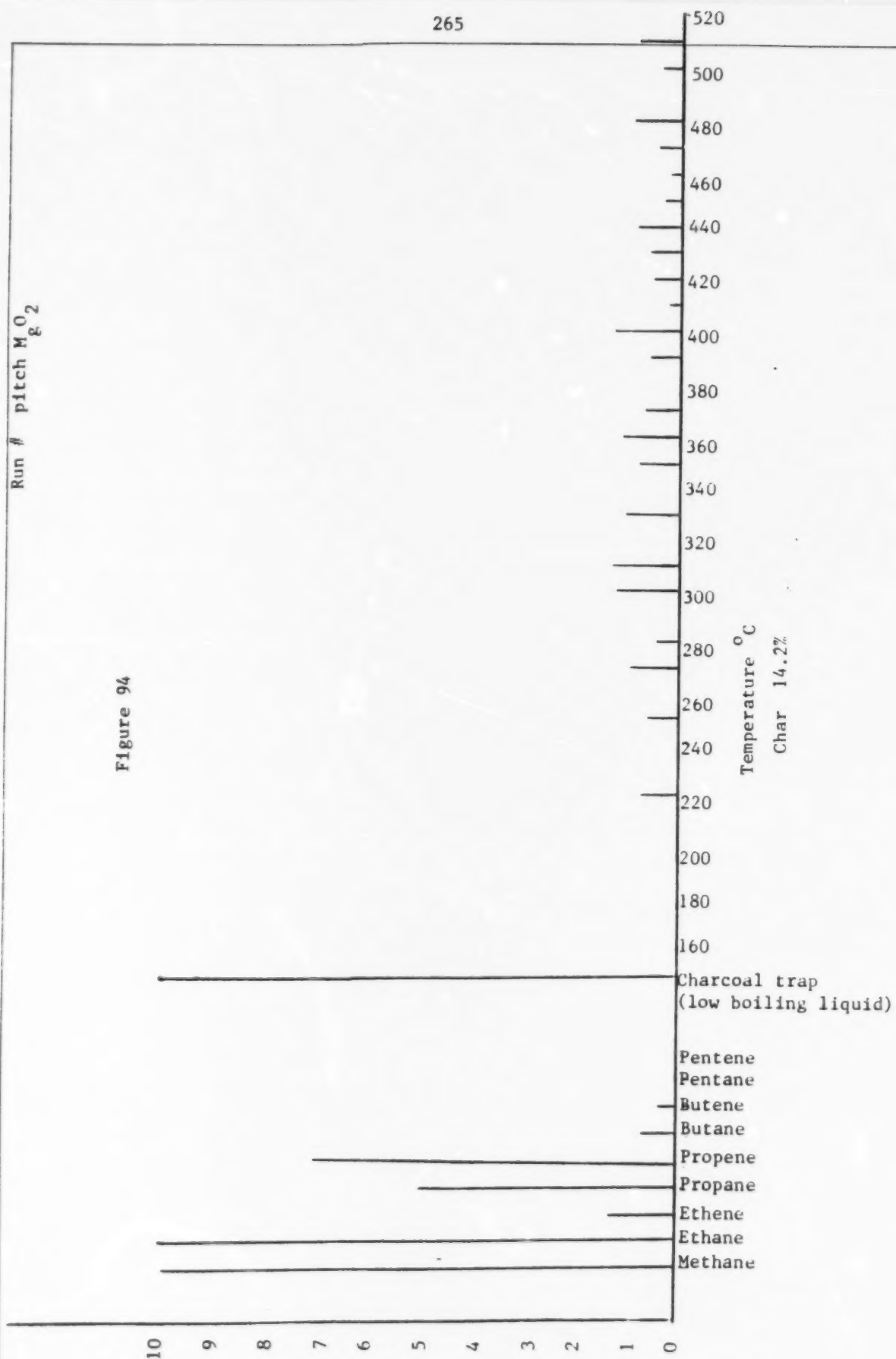
Figure 92



Run # pitch MgO_2

Figure 93





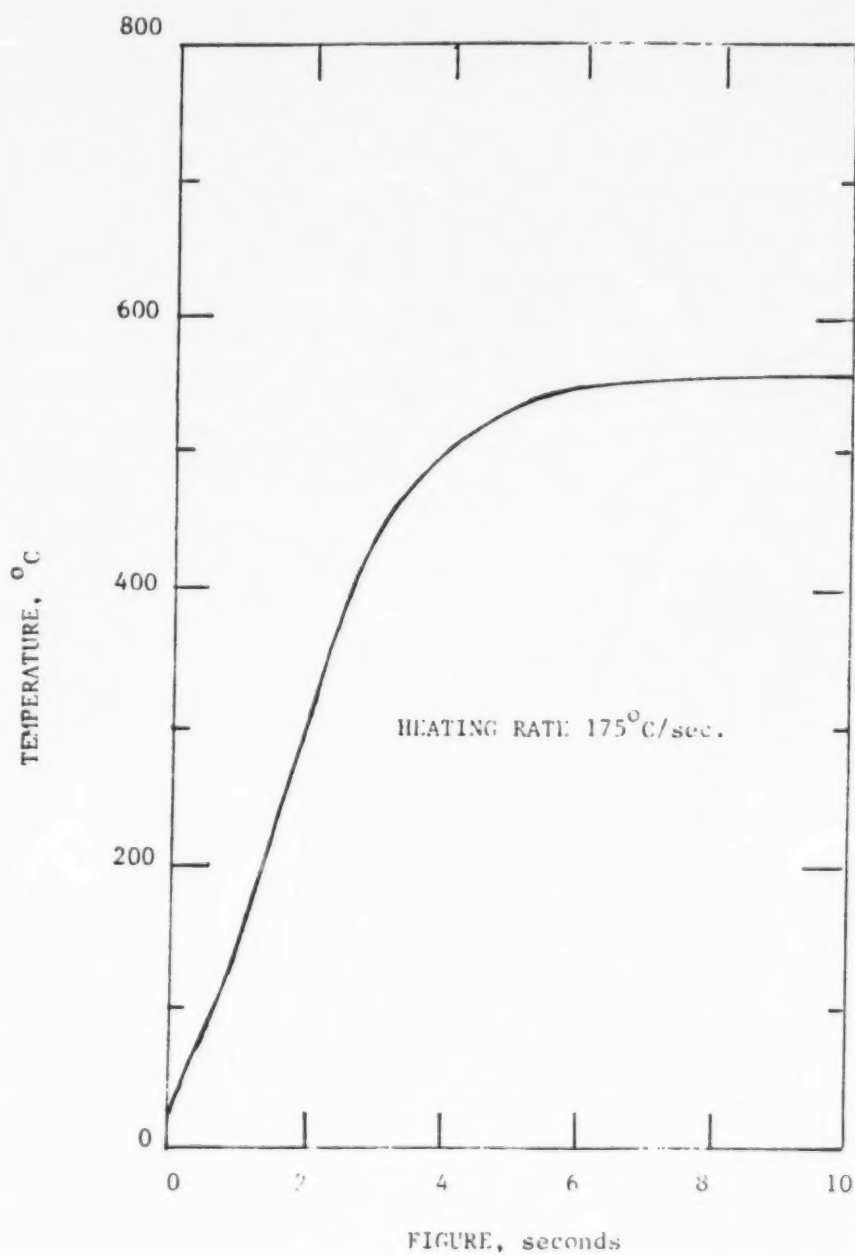


FIGURE 95: Reactor temperature versus time curve. Run No. Pitch Mg 01.

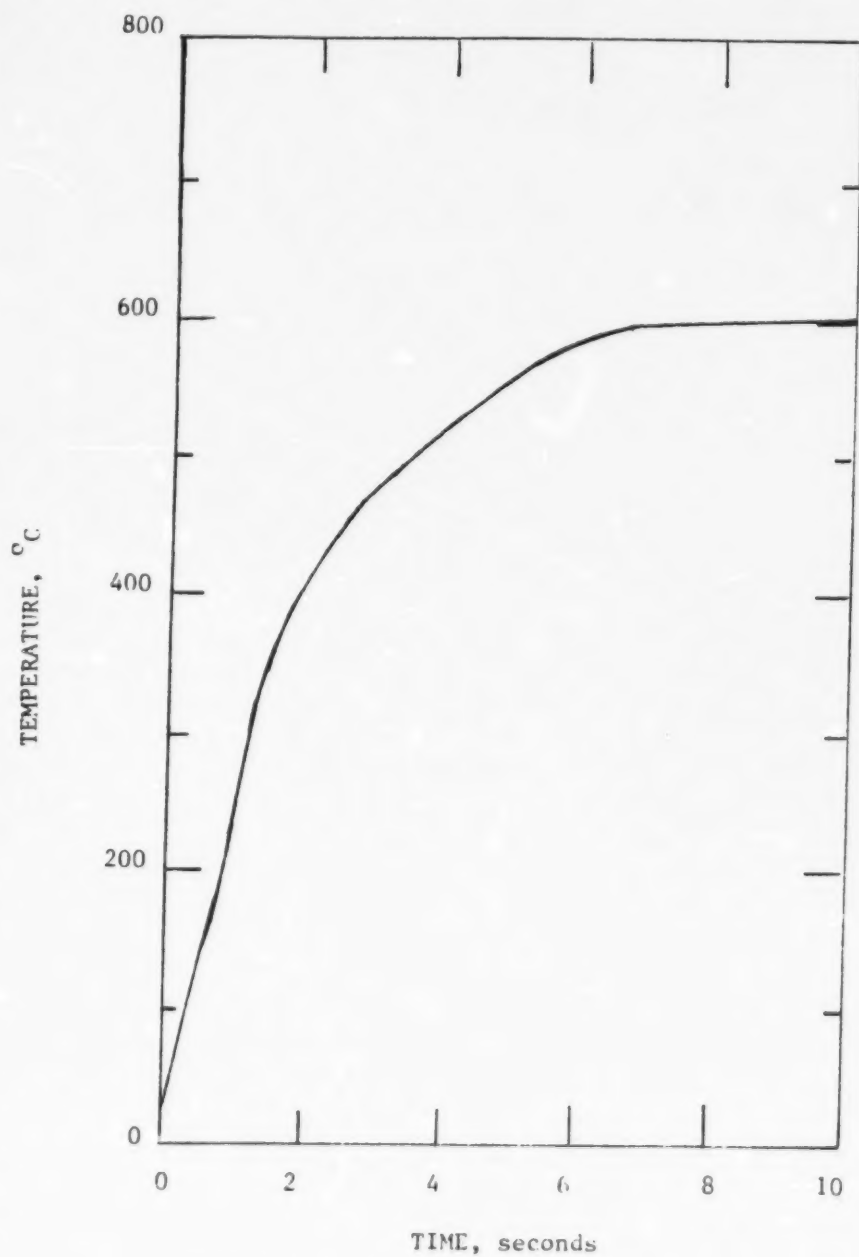


FIGURE 96: Reactor temperature versus time curve. Run No. Pitch Mg 02.

V.7 Results of Al-SiO₂
Catalyzed Experiments

Table 33 : Summary of Run Conditions and
Grouped Product Yields

	Run #	pitch AlO ₄
Catalyst/pitch ratio m/m =		0.246
Maximum Temperature oC =		475
Heating Rate oC sec. =		180
H2 pressure psi =		1,000
residence time sec. =		
mass pitch mg =		61
mass pitch mg C =		50.2
mass catalyst mg total =		15

Product	% of total C
methane	8.9
ethane	9.2
ethene	1.8
propane	7.1
propene	0.9
butane	0.7
butene	0.4
pentane	-
pentene	-
other	-
BTX liquid (light)	1.4
liquid (heavy)	31.8
* Char (residue)	20.9

* Char is whatever is left in the boat after the flash.

Table 34: Summary of Run Conditions and
Grouped Product Yields

	Run #	pitch AlO ₅
Catalyst/pitch ratio m/m =		0.195
Maximum Temperature °C =		520
Heating Rate °C sec. =		---
H ₂ pressure psi =		1,000
residence time sec. =		
mass pitch mg =		46
mass pitch mg C =		37.9
mass catalyst mg total =		9

Product	% of total C
methane	7.57
ethane	8.18
ethene	1.90
propane	7.65
propene	4.88
butane	0.84
butene	1.37
pentane	—
pentene	—
other	—
BTX liquid (light)	7.4
liquid (heavy)	28.9
* Char (residue)	20.3

* Char is whatever is left in the boat after the flash.

Table AA106: Summary of Run Conditions and Grouped Product Yields

Run # pitch A106

Catalyst/pitch ratio m/m = 0.244

Maximum Temperature ^oC = 570

Heating Rate ^oC /sec = 237

H Pressure psi = 1000

² residence time sec = 3.95

mass pitch mg = 49.0

mass pitch mg C = 40.3

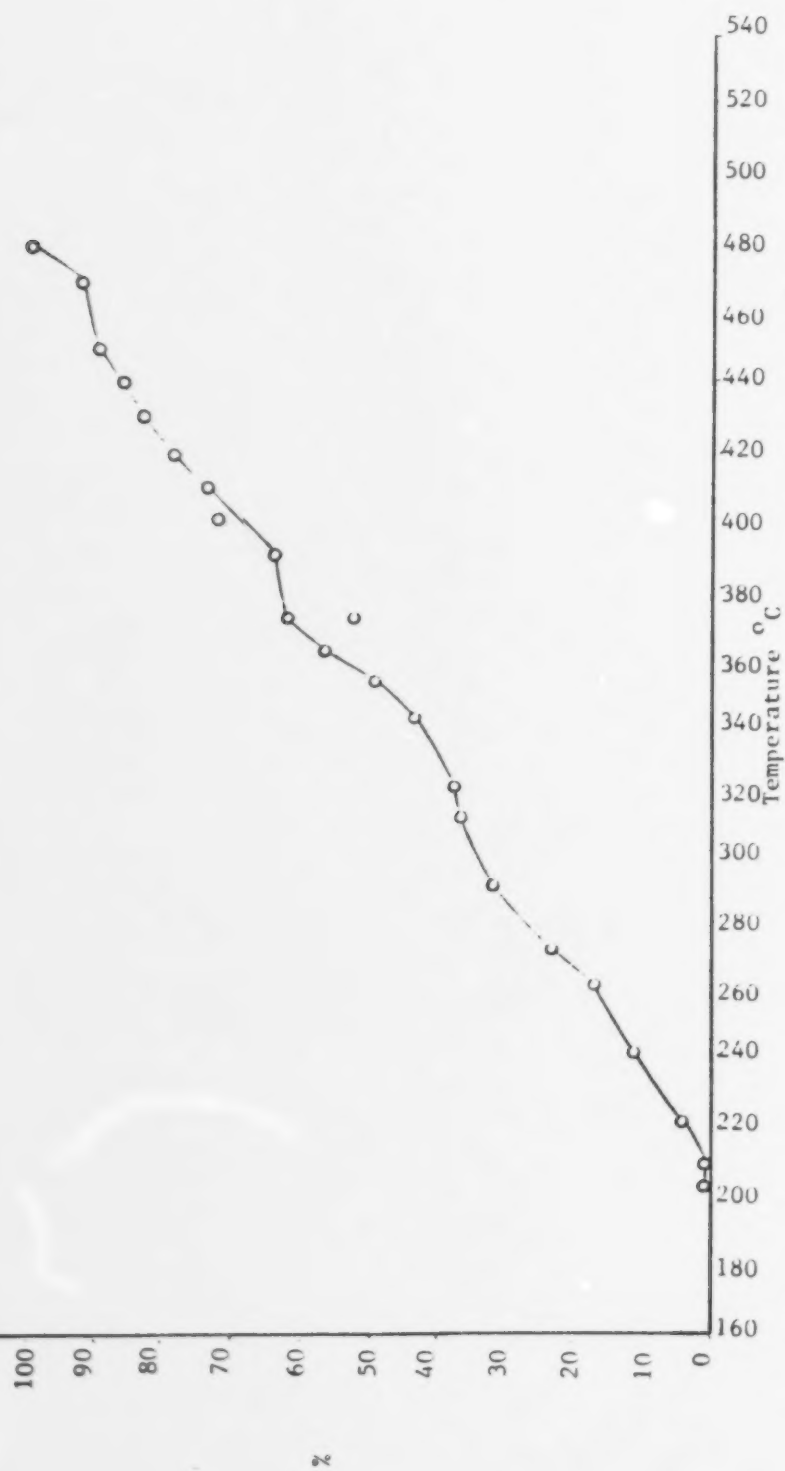
mass catalyst mg total = 12.0

Product	% of total C
C	8.7
1	
C	10.7
2	
C	17.4
3	
C	4.9
4	
C	---
5	
other	---
BTX liquid (light)	4.3
Liquid (heavy)	21.8
* Char (residue)	---

* Char is whatever is left in the boat after the flash.

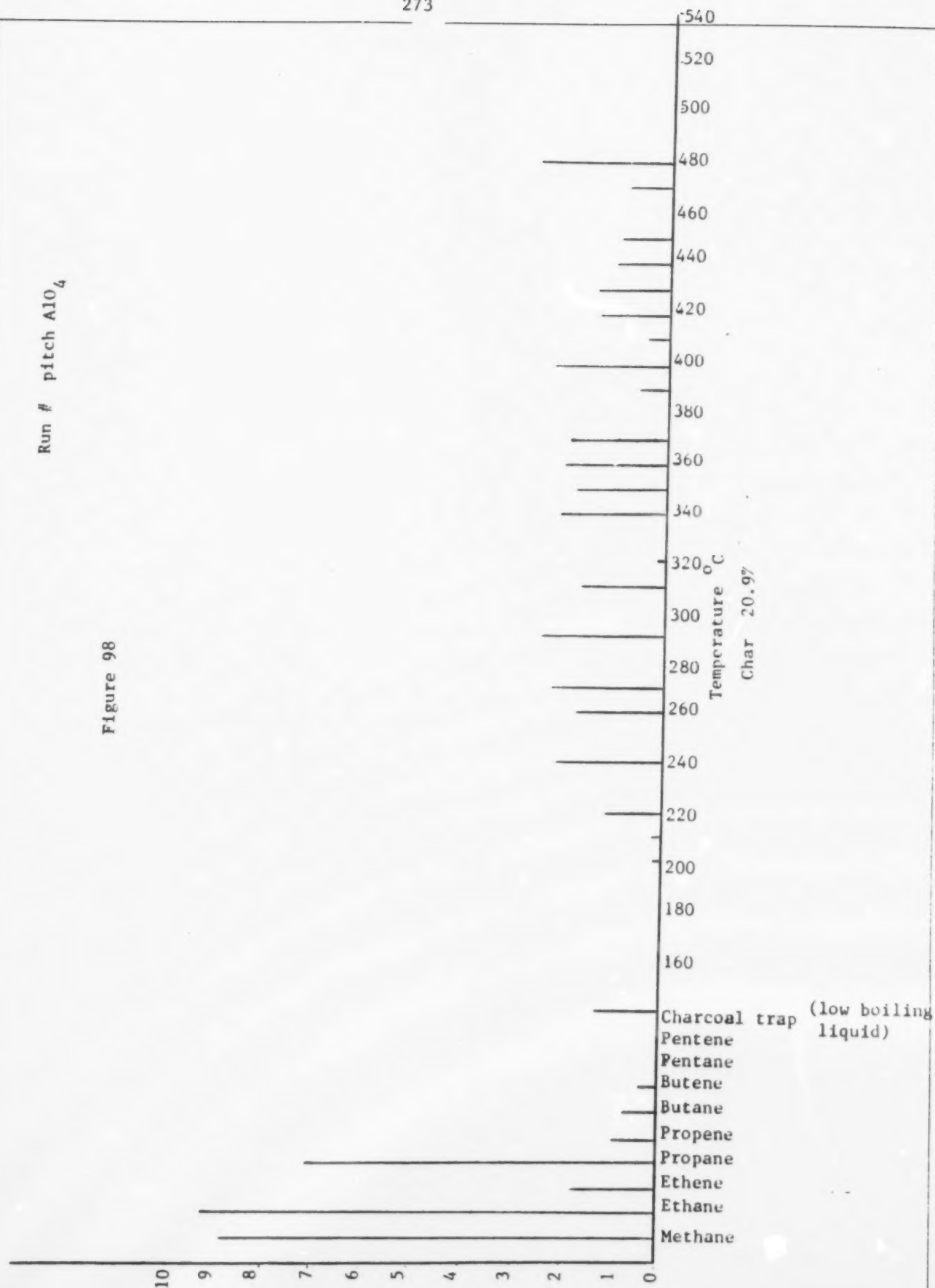
Run # pitch AlO_4

Figure 97



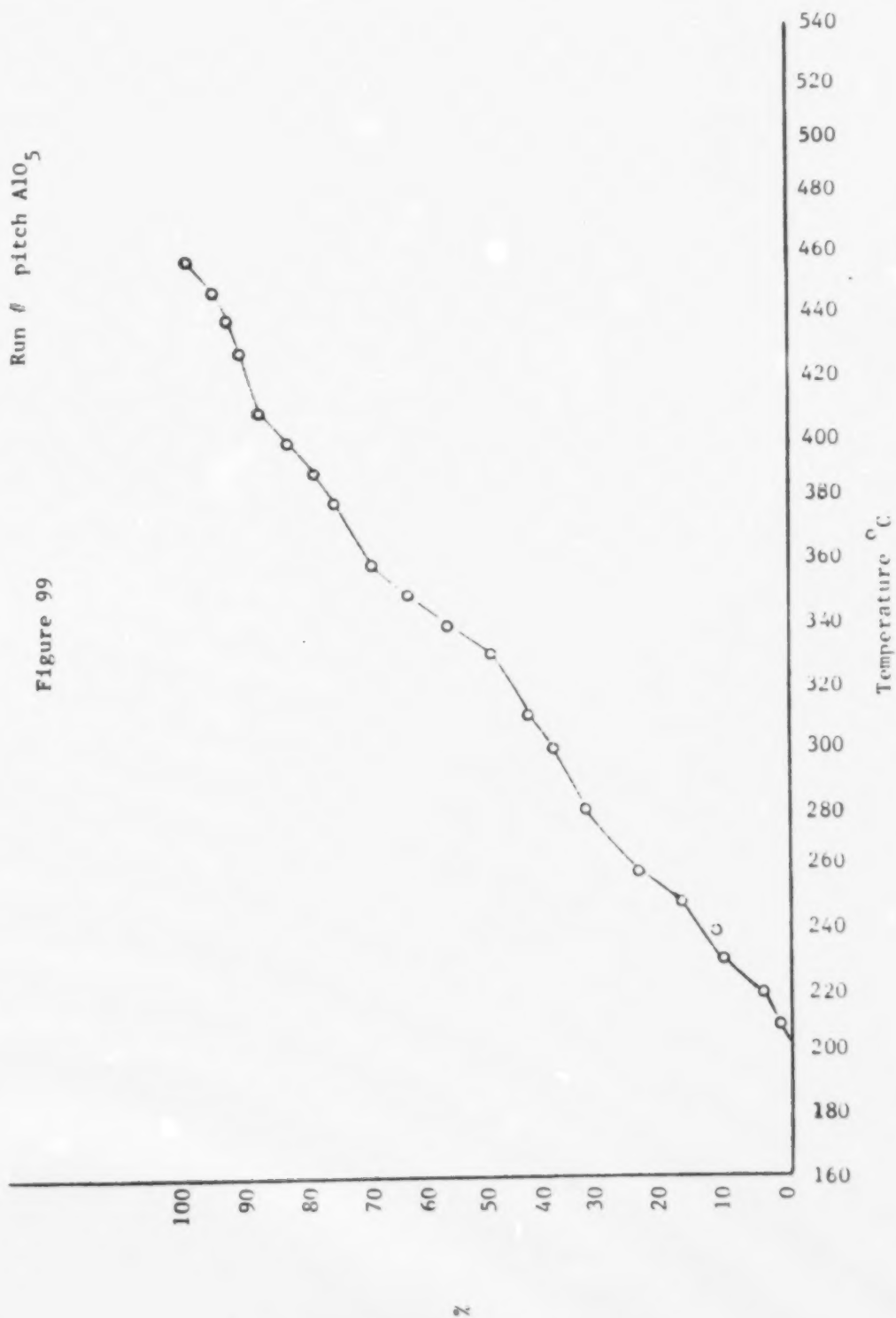
Run # pitch AlO₄

Figure 98



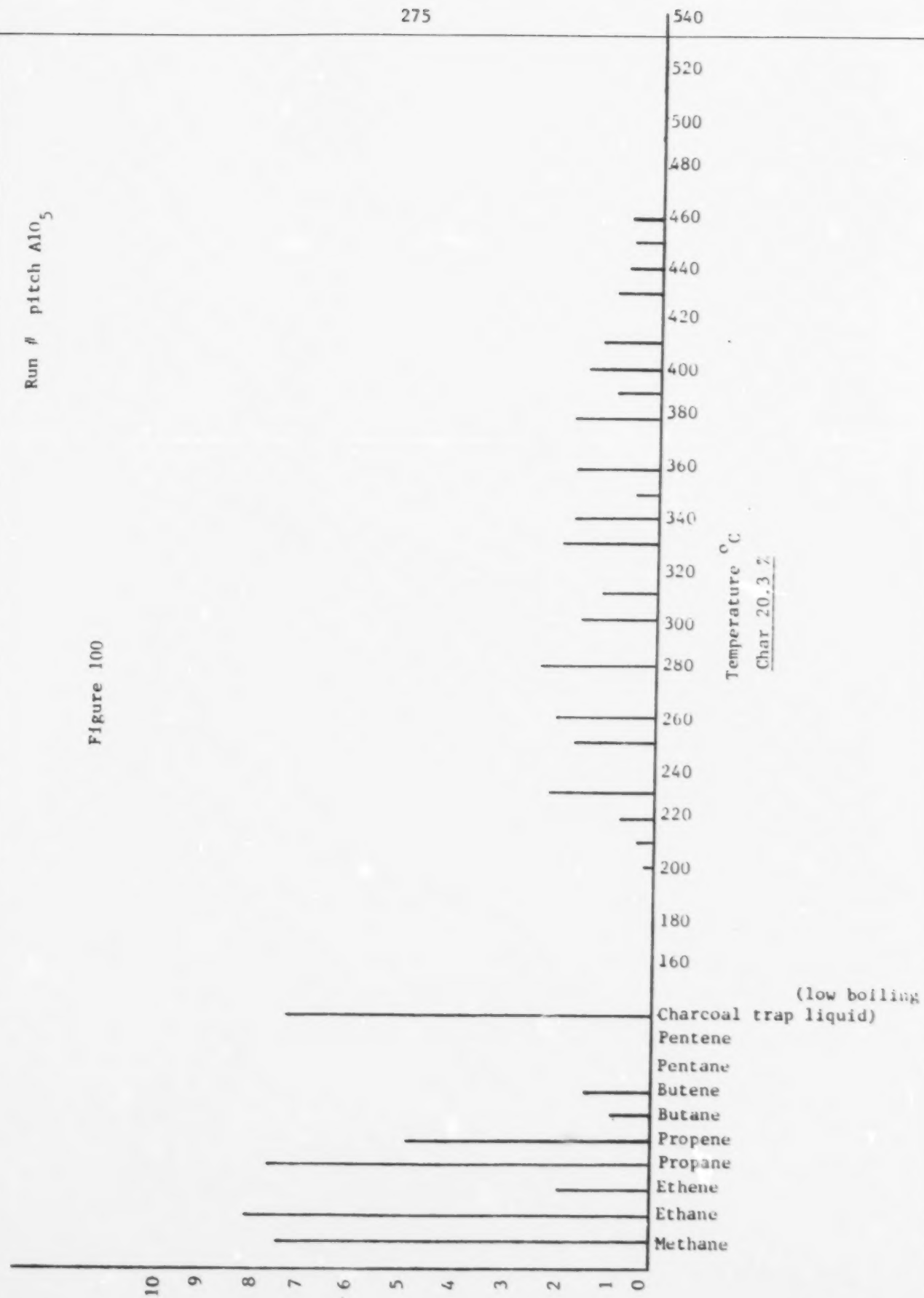
Run # pitch A10₅

Figure 99



Run # pitch A10₅

Figure 100



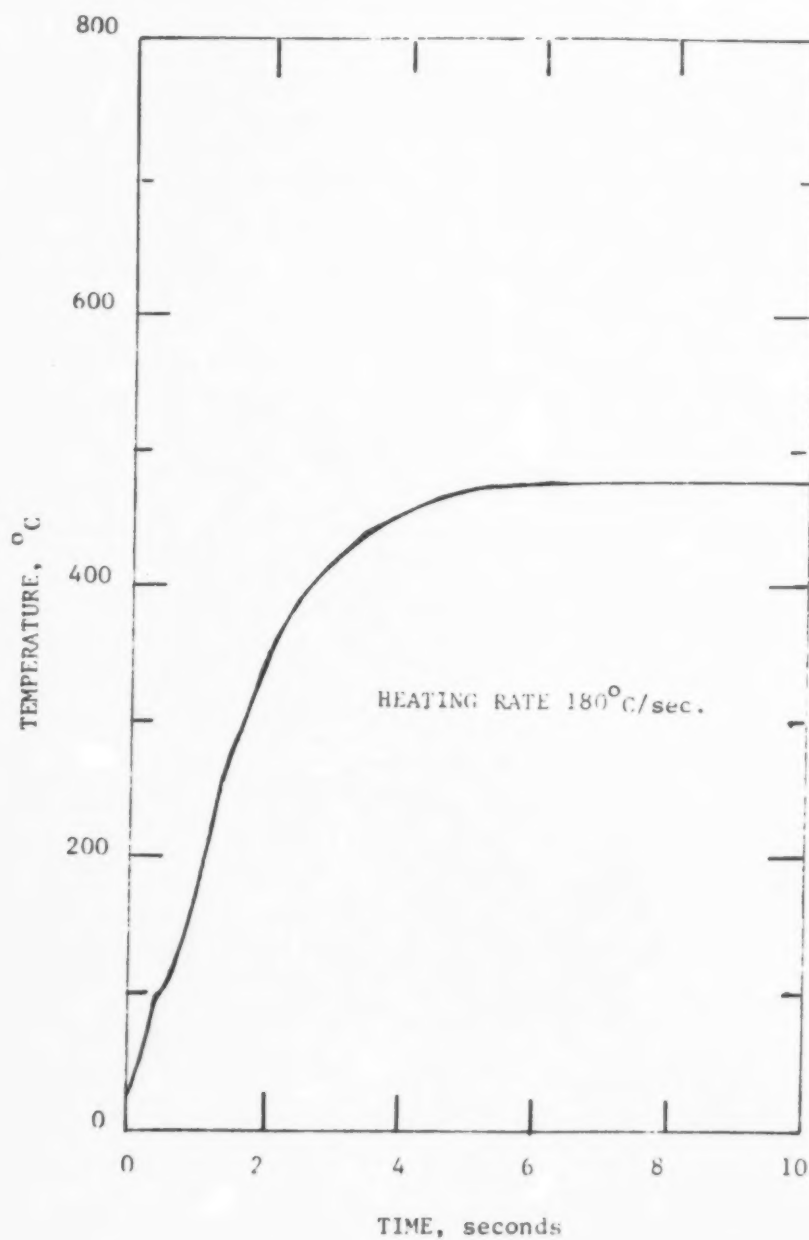


FIGURE 101: Reactor temperature versus time curve. Run No. A1 04.

V.8 Results of P-SiO₂
Catalyzed Experiments

Table 35: Summary of Run Conditions and
Grouped Product Yields

Run #	pitch PQ ₁
Catalyst/pitch ratio m/m =	0.228
Maximum Temperature °C =	546
Heating Rate °C sec. =	275
H ₂ pressure psi =	1,000
residence time sec. =	3.95
mass pitch mg =	57
mass pitch mg C =	46.9
mass catalyst mg total =	13

Product	% of total C
methane	16.4
ethane	17.2
ethene	2.0
propane	7.3
propene	4.2
butane	1.4
butene	7.2
pentane	—
pentene	—
other	—
BTX liquid (light)	5.2
liquid (heavy)	20.7
* Char (residue)	19.8

* Char is whatever is left in the boat after the flash.

Table AP02: Summary of Run Conditions and
Grouped Product Yields

Run # pitch P02

Catalyst/pitch ratio m/m = 0.254

Maximum Temperature ^oC = ---

Heating Rate ^oC /sec = ---

H Pressure psi = 1000

² residence time sec = 3.95

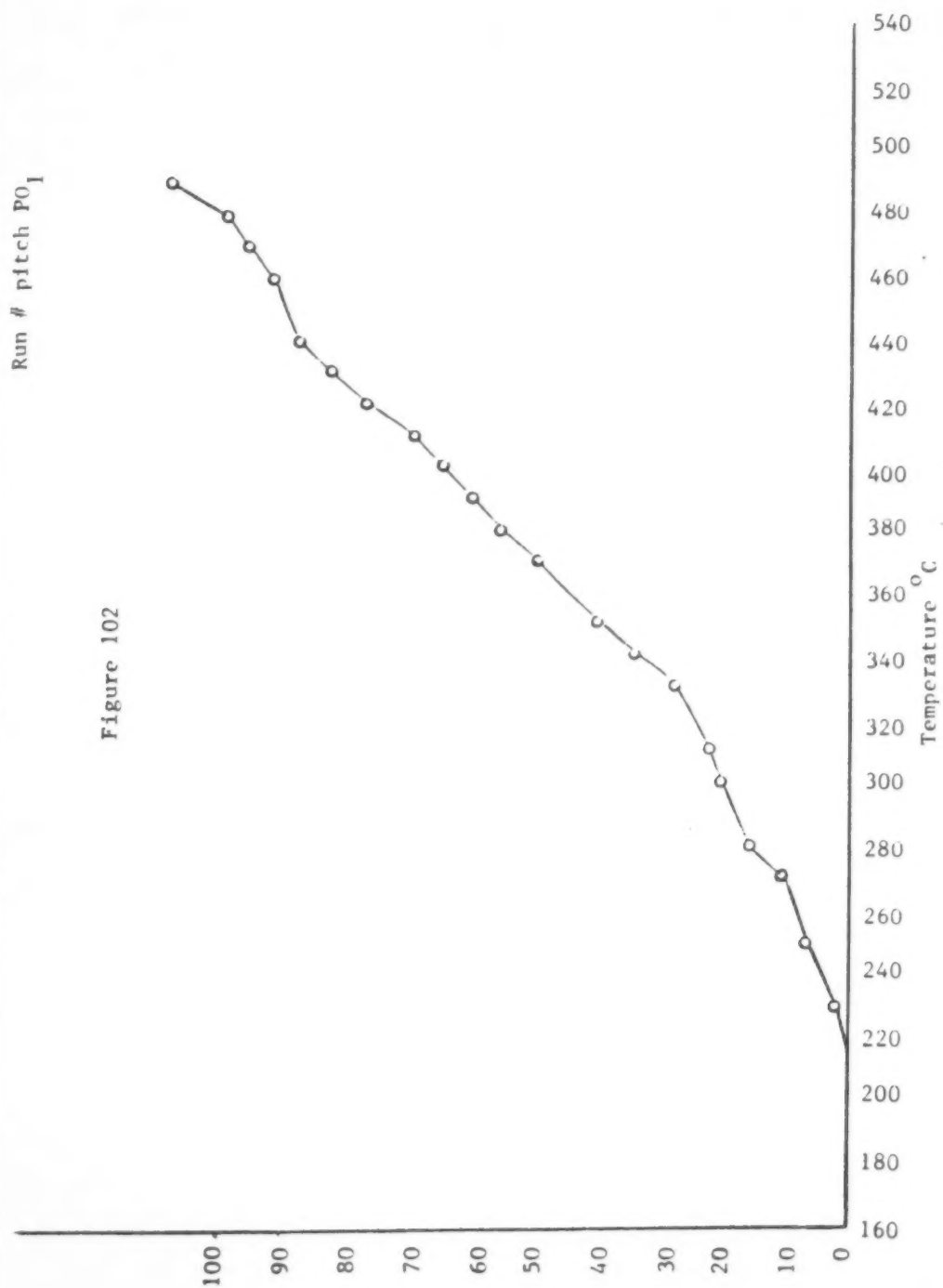
mass pitch mg = 51.0

mass pitch mg C = 42.0

mass catalyst mg total = 13.0

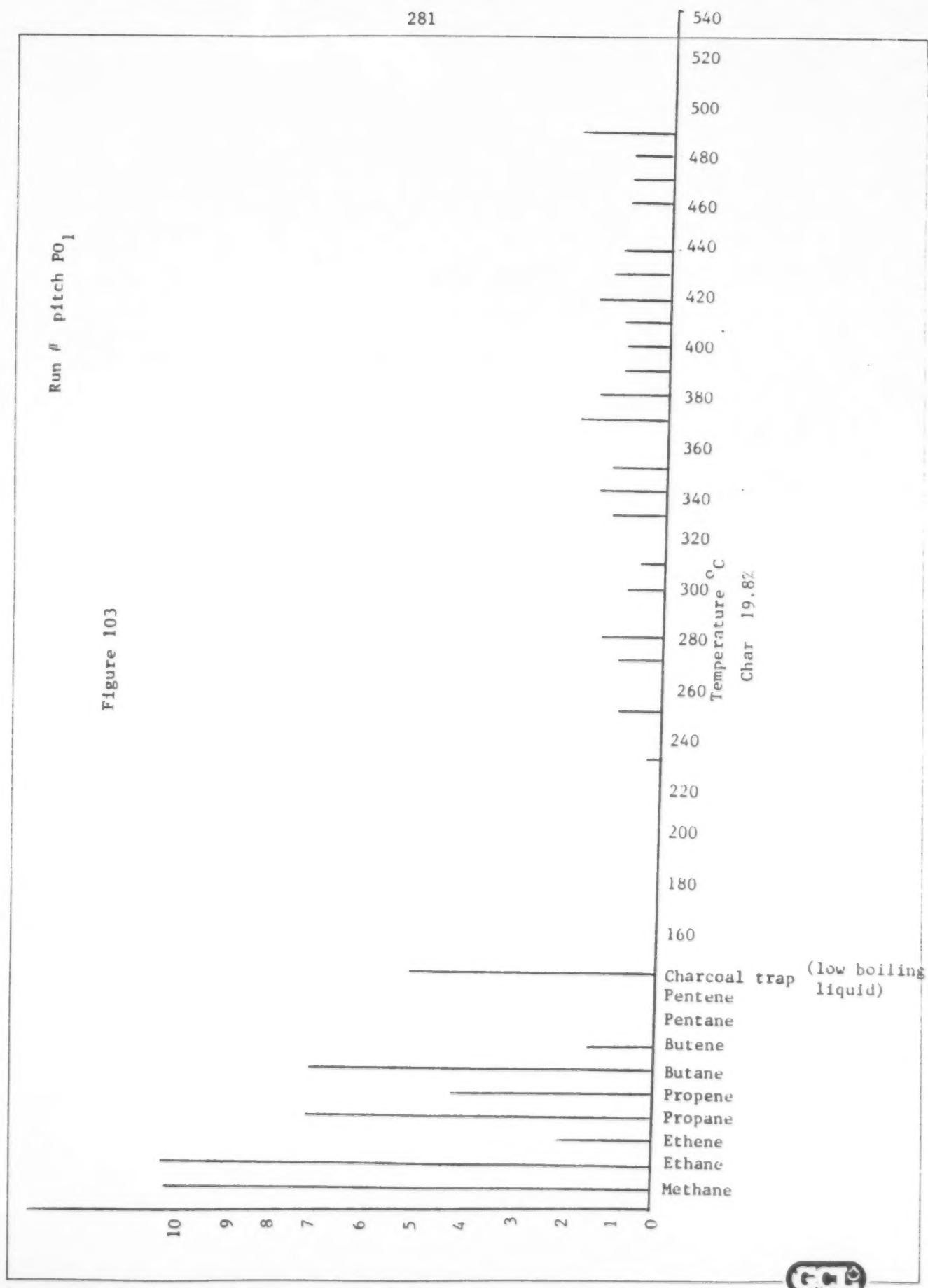
Product	% of total C
C	3.0
1	
C	4.5
2	
C	6.5
3	
C	2.2
4	
C	0.3
5	
other	---
BTX liquid (light)	19.5
Liquid (heavy)	27.1
* Char (residue)	26.9

* Char is whatever is left in the boat after the flash.



Run # pitch PO₁

Figure 103



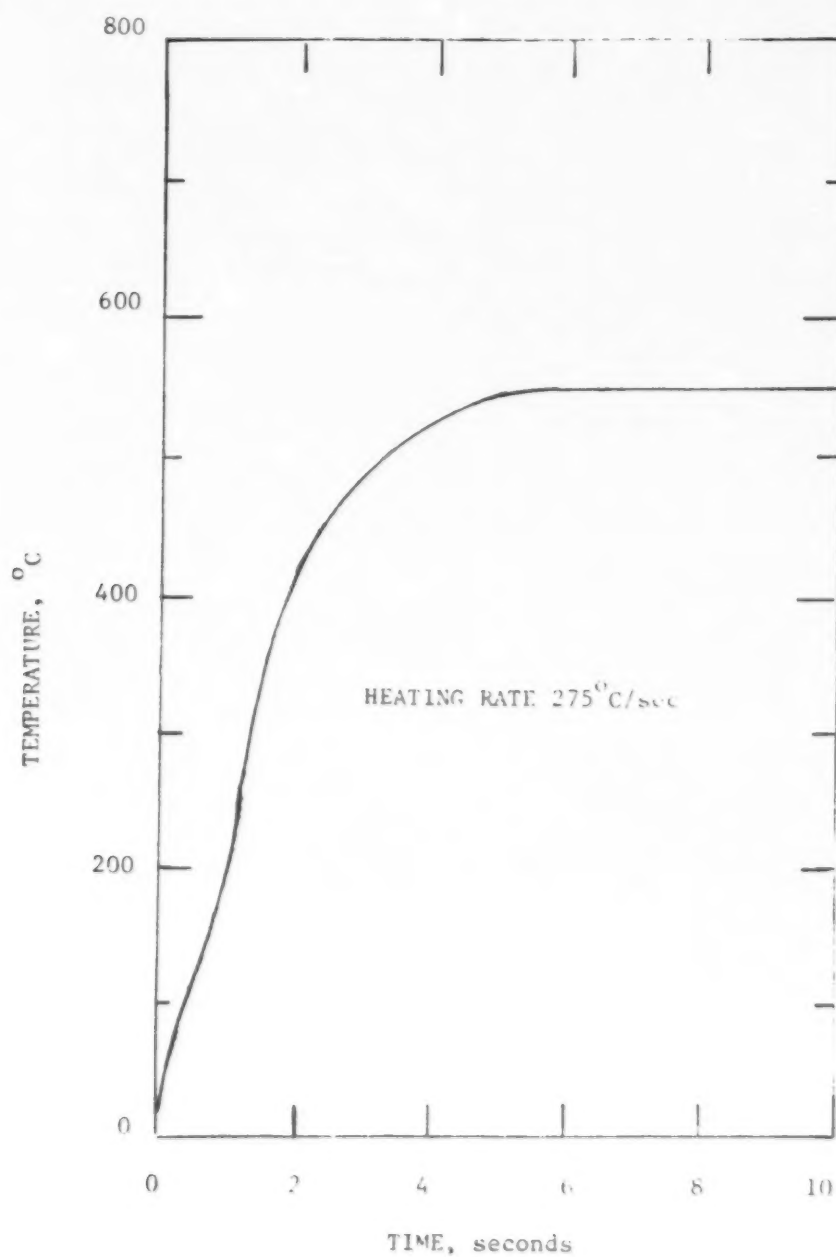


FIGURE 104: Reactor temperature versus time curve. Run No. Pitch P 01

V.9 Results of Na-SiO₂
Catalyzed Experiments

Table 36

Run number	pitch Na01
Catalyst/pitch ratio m/m	.196
Maximum Temperature ^o C	522
Heating Rate ^o C sec.	261
H ₂ pressure psi	1000
Residence time sec.	3.95
Mass pitch mg	56
Mass pitch mg C	46.1
Mass catalyst mg total	11

	% of Total C

Methane	22.1
Ethane	20.8
Ethene	1.5
Propane	7.4
Propene	2.3
Butane	0.9
Butene	0.4
BTX liquid (light)	6.6
Liquid (heavy)	29.1
*Char (residue)	<u>17.4</u>
Total	108.5

*Char is whatever is left in the boat after the flash.

Table ANa02: Summary of Run Conditions and Grouped Product Yields

Run # pitch Na02

Catalyst/pitch ratio m/m = 0.189

Maximum Temperature $^{\circ}\text{C}$ = 558

Heating Rate $^{\circ}\text{C} / \text{sec}$ = 213

H Pressure psi = 1000

₂ residence time sec = 3.95

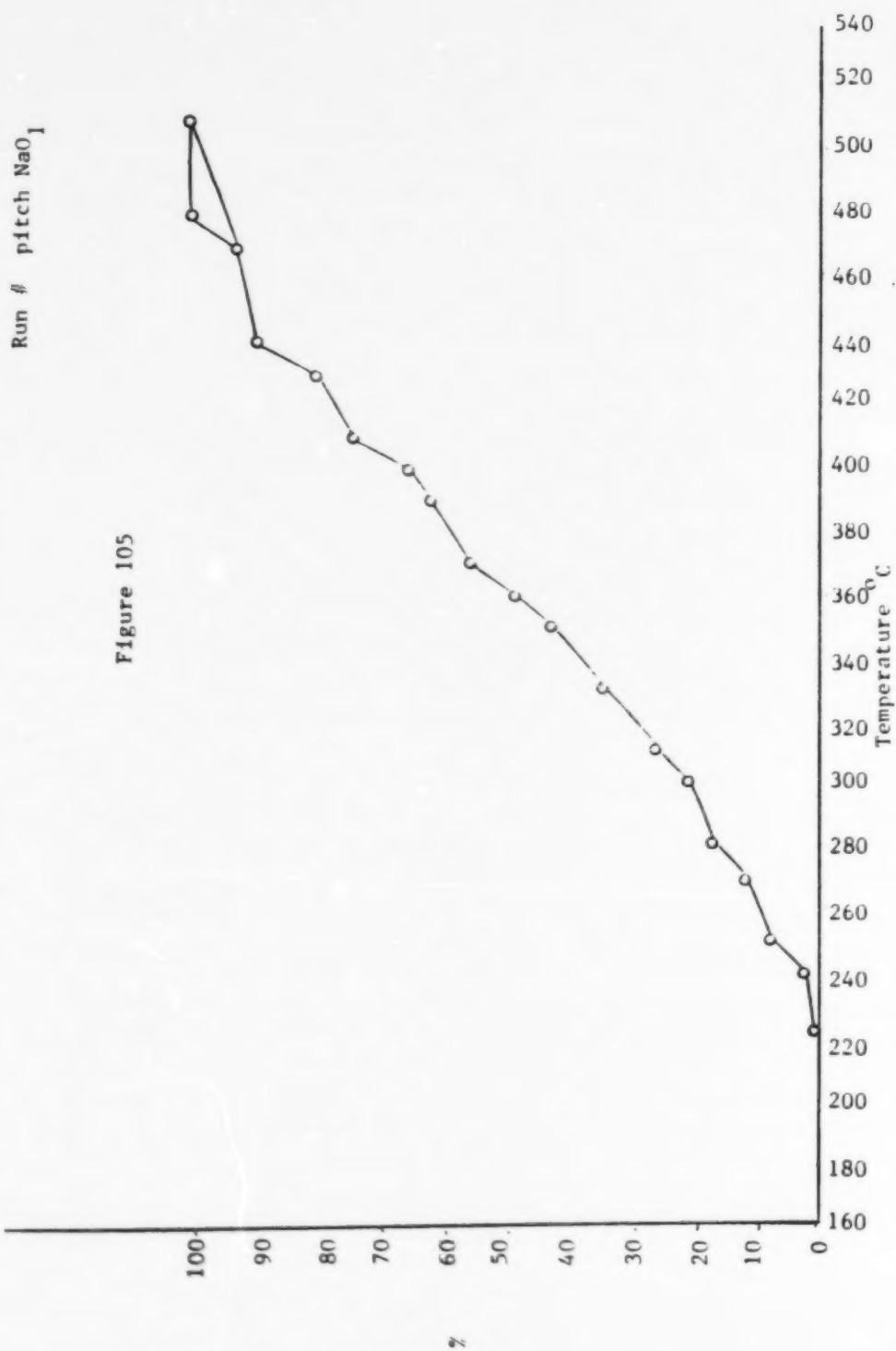
mass pitch mg = 58.0

mass pitch mg C = 11.0

mass catalyst mg total = 47.7

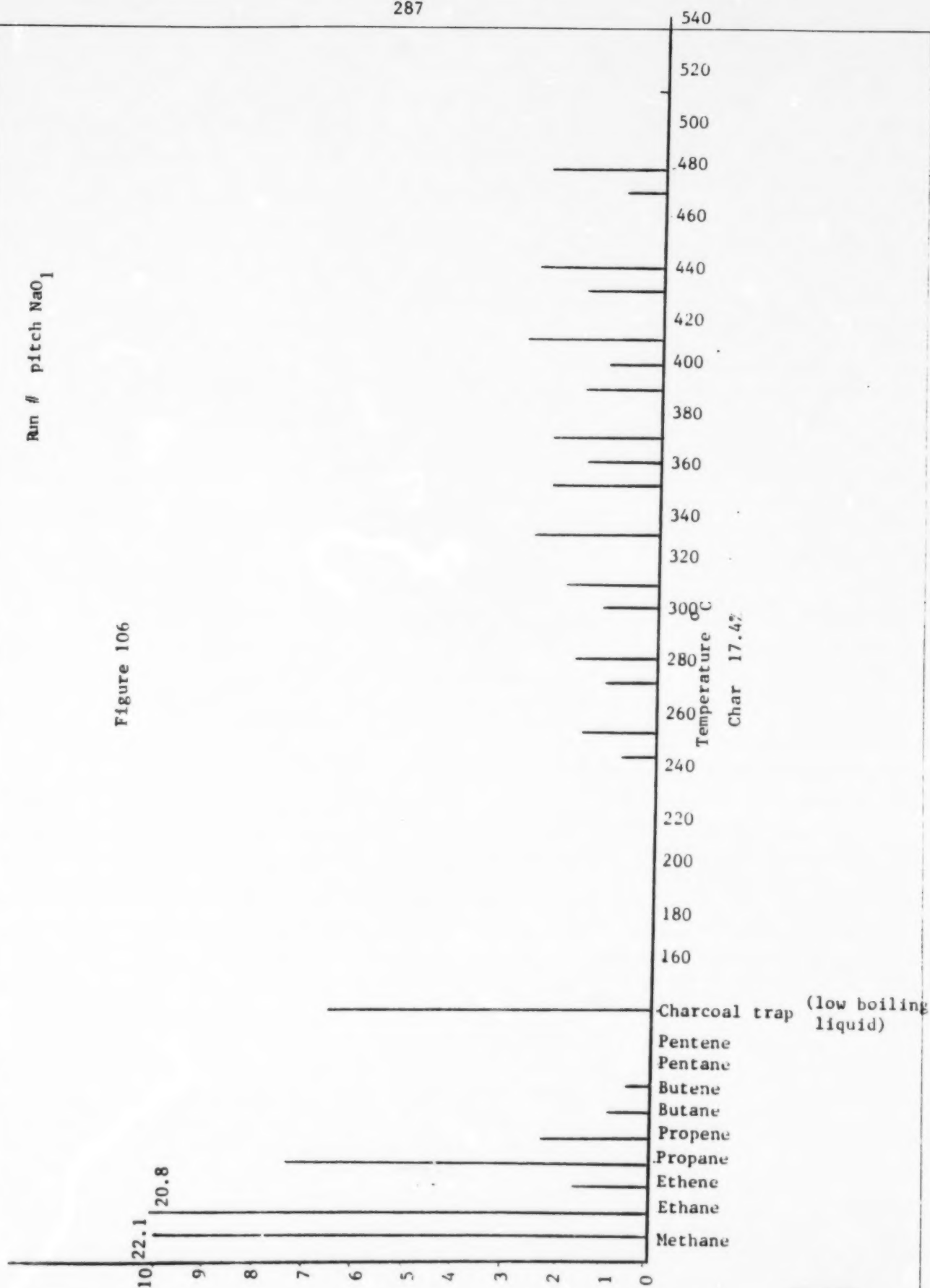
Product	% of total C
C	10.0
1	
C	11.9
2	
C	13.1
3	
C	1.6
4	
C	1.3
5	
other	0.1
BTX liquid (light)	28.4
Liquid (heavy)	17.3
* Char (residue)	17.8

* Char is whatever is left in the boat after the flash.



Run # pitch NaO₁

Figure 106



V.10 Results of KCl
Catalyzed Experiments

Table 37

Run Number	Pitch K01
Catalyst/pitch ratio m/m	0.59
Maximum temperature °C	598
Heating Rate °C sec.	240
H ₂ pressure psi	1000
Residence time sec.	3.95
Mass pitch mg	49
Mass catalyst mg C	40.3
Mass catalyst mg total	29

	% of Total C

Methane	8.0
Ethane	8.5
Ethene	2.0
Propane	5.9
Propene	3.2
Butane	1.1
Butene	0.8
BTX liquid (light)	3.6
Liquid (heavy)	41.1
*Char (residue)	<u>25.7</u>
Total	95.4

*Char is whatever is left in the boat after the flash.

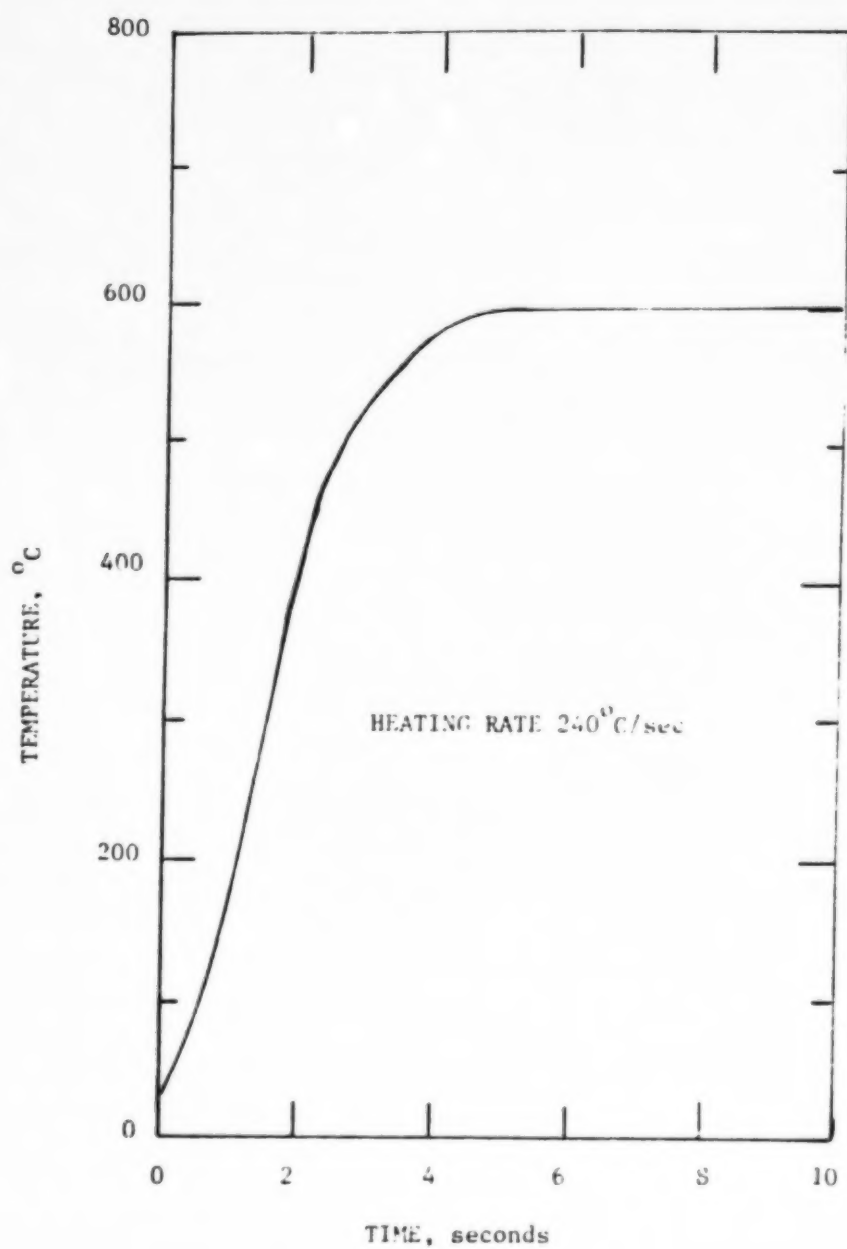


FIGURE 107: Reactor temperature versus time curve. Run No. Pitch K 01

V.11 Results of CaCl_2
Catalyzed Experiments

Table 38

Run Number	Pitch Ca01
Catalyst/pitch ratio m/m	0.51
Maximum Temperature ^o C	617
Heating Rate ^o C sec.	220
H ₂ pressure psi	1000
Residence time sec.	3.95
Mass pitch mg	39
Mass pitch mg C	32.1
Mass catalyst mg total	20

	% of Total C

Methane	8.0
Ethane	8.3
Ethene	4.0
Propane	7.0
Propene	4.3
Butane	1.0
Butene	1.7
BTX liquid (light)	5.4
Liquid (heavy)	37.1
*Char (residue)	22.0

Total	98.8
*Char is whatever is left in the boat after the flash.	

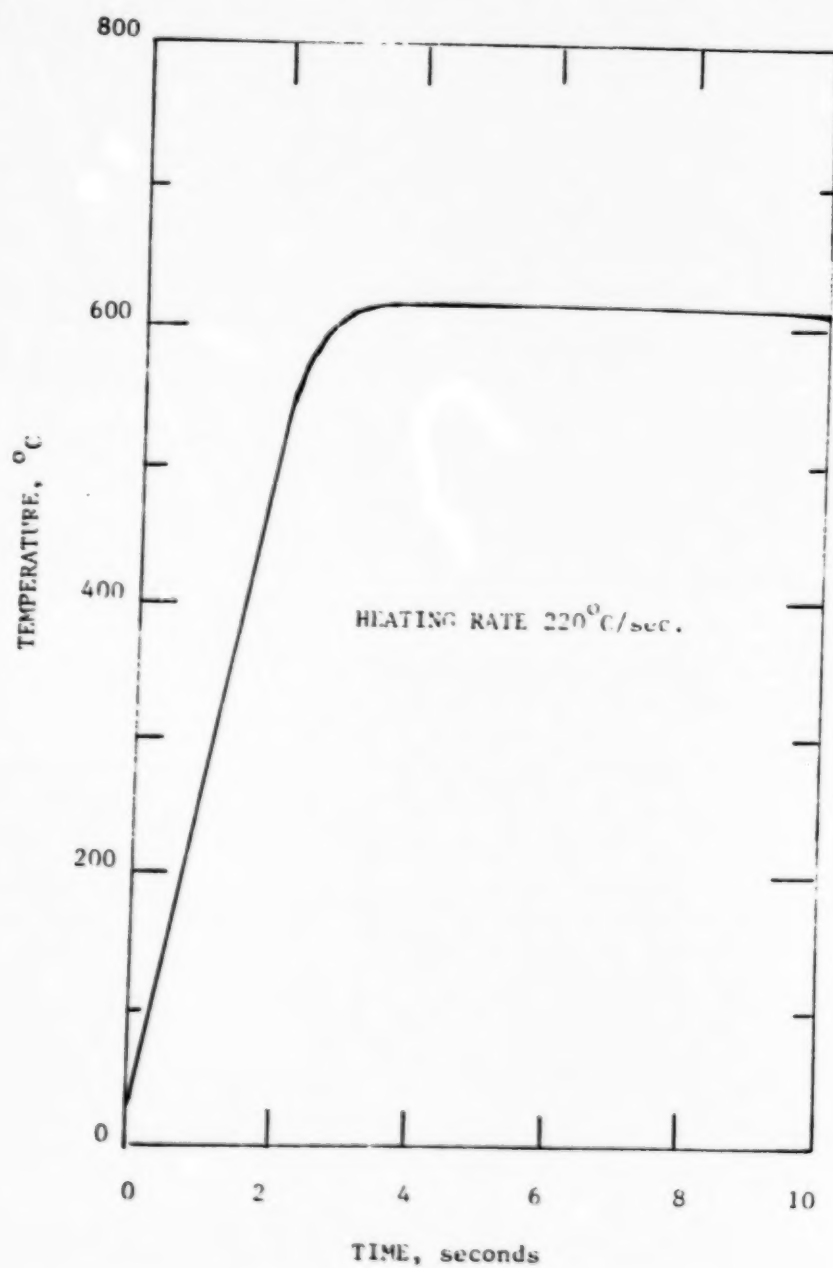


FIGURE 102: Reactor temperature versus time curve. Run No. Pitch Ca 01

VI CONCLUSIONS

A comparison of non-catalytic and catalytic results of this investigation show that catalytic FHP is necessary to reduce char formation, which is often produced as an unwanted by-product. The results reported here suggest that process variables cause several effects. It would appear that short residence times in the solid phase are necessary to avoid polymerization and that short residence times in the vapour phase are necessary to avoid secondary reactions. In order to have high conversions at short residence times, very fast heating rates are essential. However if the heating rates are too fast, secondary reactions will occur before volatilization. Similarly if the final reaction temperature is too high secondary reactions will occur before the products leave the reactor. While the catalyst enhances both cracking reactions and hydrogenation reactions, excessive amounts will also enhance secondary reactions.

The fact that the hydrogen pressure seems to have only a minor influence on the product distribution is important. It suggests that a flash hydrolysis process might produce reasonably high conversions at pressures as low as 1.8 MPa (250 psig). This pressure is almost an order of magnitude lower than the pressures being used to hydrocrack residual oils. If lower pressures could be used, there might be a significant decrease in the investment capital

required to construct an upgrading plant.

Corrosion from chloride catalysts is a genuine concern. However if the capital cost savings from decreased pressure was sufficient, special corrosion resistant materials might be justified in the low temperature portion of the plant where condensation of moisture could occur.

VII RECOMMENDATIONS

Conversion of Cold Lake Pitch
To Lower Boiling Distillates in a
Two-Stage Continuous Flash Hydropyrolytic Reactors

Description of Appartus

The proposed apparatus for flash hydropyrolysis (FHP) of pitch is shown in Figure 110. The pitch mixed with catalyst ZnCl_2 (Pitch: ZnCl_2 wt. ratio 1-2) will be fed by a suitable pump (through a heated line at 100-150 °C) at a rate of 1-10 mL/min to the top of the reactor at 600 °C. The reactor will be made of heavy-wall stainless steel tube of 1/2" diameter and 12" long and will contain stainless steel screen baffles of 30 mesh size. The reactor tube will be enclosed in a high temperature furnace. The temperature of the furnace will be controlled by a temperature controller. The reactor temperature will be measured at three points along the axis and at the inlet and exit locations. The hydrogen gas will be fed at high pressure (1,000-2,000 psi) at a flow rate of 570 mL/min at the top of the reactor after passing through a mass flow meter (Matheson, 3,000 psi). A high pressure relief valve will be provided for safe operation against high pressure. The ash and coke containing solid products of pyrolysis will be collected at the bottom of the reactor into a separate vessel. The vapour phase products of the FHP reactor will be passed through a series of cooling traps and a back pressure regulator for GC analysis. Under an alternative scheme, the vapour phase products of FHP reactor will be passed through

another reactor containing zeolite ZSM-5 for further upgrading via hydrocracking and reforming. The products obtained from the zeolite reactor will be passed through traps and a gas chromatograph. The zeolite reactor will be made of 3/4"OD, 8 in. long stainless steel tube and will be equipped with individual temperature control and measurement devices. The operating temperature will be maintained in the range 400-500 °C.

Feeding of Pitch

Many options are available for the design of feeding mechanism of pitch and catalyst ZnCl_2 to the high pressure reactor.

Option 1 The pitch is mixed with zinc chloride in a separate container connected to a screw feeder pump. The high pressure screw pump feeds the pitch- ZnCl_2 mixture to the reactor. The amount of mixture fed to the reactor can be estimated by the difference in the weight of the container measured during a specified time period. A schematic of the Option 1 is given in Figure 111.

Option 2 The pitch is mixed with ZnCl_2 and loaded into the barrel of a piston pump (as shown in Figure 112) to be fed to the reactor. The barrel should have enough capacity to contain the pitch and ZnCl_2 mixture required for the entire experiment. The piston is moved by gears driven by motor.

Option 3 Under this option, the pitch and ZnCl_2 are fed separately into the reactor from separate feeding mechanisms. Either a screw pump or a piston pump as in options 1 and 2 can be used.

Legend for Figure

AC	Ash - coke collector
CV	Check valve
F	Furnace
GC	Gas chromatograph
HTR	High temperature trap
MF	Mass flow meter
NV	Needle valve
P	Pump for feeding pitch
PG	Pressure gauge
PR	Pitch pyrolyzer-reactor
RV	Relief Valve
SV	Shut off valve
T	Thermocouple
TCI	Temperature controller - indicator
TR	Cooling trap
ZR	Zeolite reactor
Heated tube	
BPR	Back pressure regulator
TWV	Three way valve

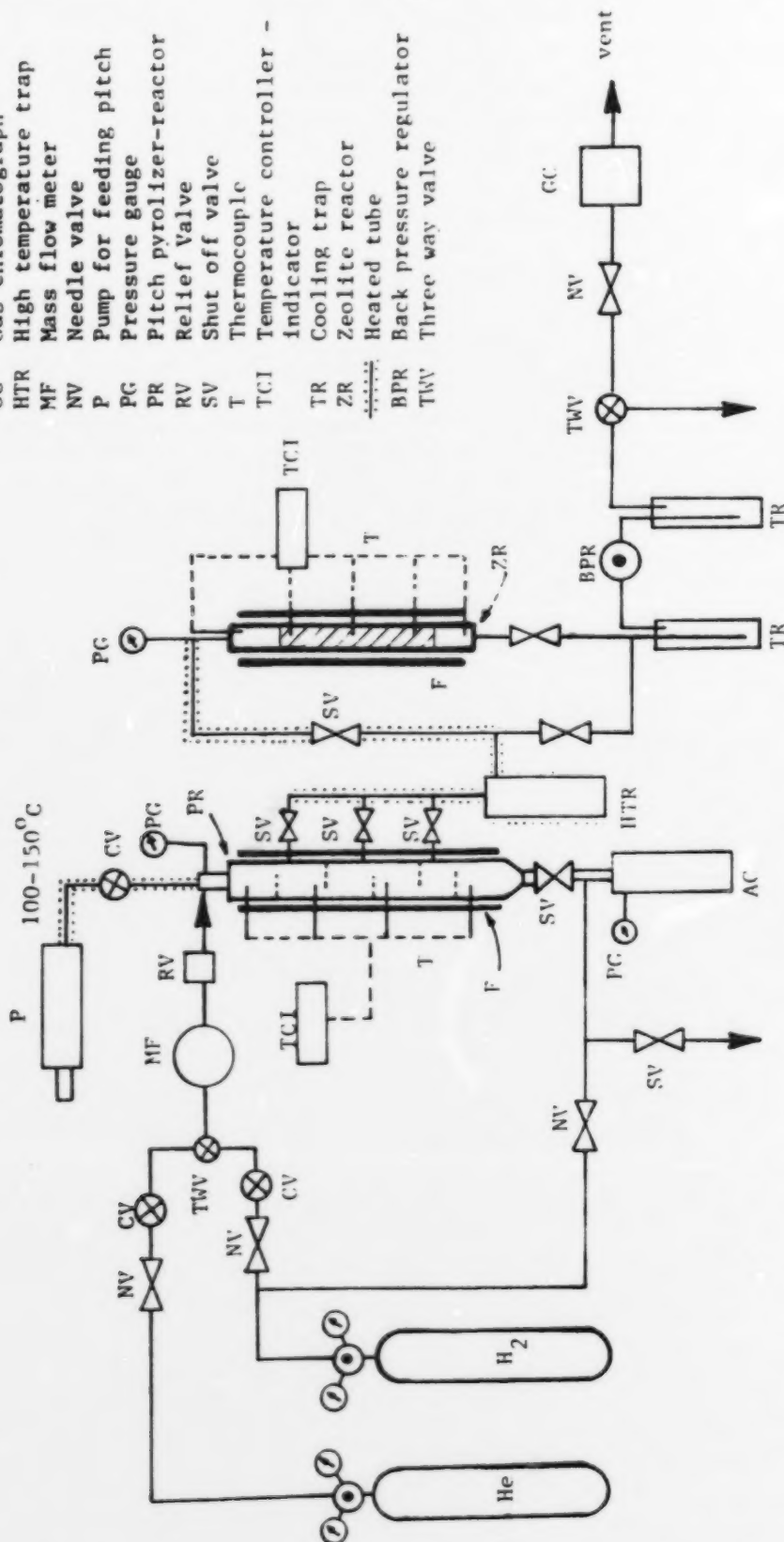


FIGURE: 110 Schematic diagram of PP apparatus

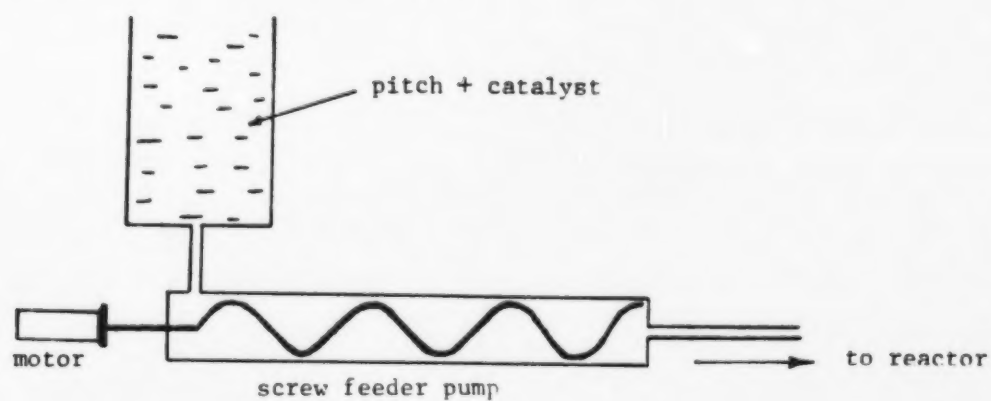


FIGURE 111: OPTION 1

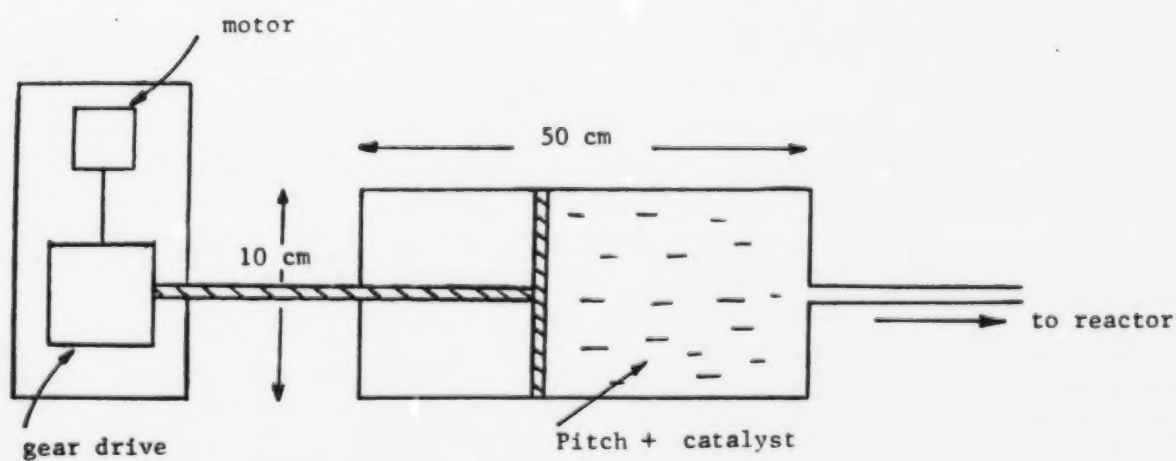


FIGURE 112: OPTION 2

VIII REFERENCES

REFERENCES

1. R. N. Pandey, "Development and Evaluation of Catalysts for Hydrogenation of Condensed Polynuclear Aromatic Compounds," Guelph Chemical Laboratories Ltd., Report to CANMET, 1982.
2. H. Juntgen, "Zum Mechanismus Von Pyrolyse Und Hydropyrolyse," Erdöl und Kohle 38, 448, 1985.
3. F. Mondragon et al, "Coal Liquefaction by the Hydrogen Produced from Methanol," Fuel, 61, 392, 1982.
4. F. Mondragon et al, "Coal Liquefaction by the Hydrogen Produced from methanol. 2 Model Compound Studies," Fuel, 63, 579, 1984.
5. R. J. Belt and L. A. Bissett, "Assessment of Flash Pyrolysis and Hydropyrolysis," METC/RI-79/2, Morgantown Energy Technology Centre, Morgantown, WV, July 1978.
6. E. F. Woodburn et al, "Thermal decomposition and hydrogenation of coal dust in a shock tube," Fuel, 53, 38, 1974.
7. K. C. Channabasappa, "Hydrogenolysis of Bituminous Coal, Institute of Gas Technology, Chicago, Illinois, 48, 1956.
8. R. W. Hiteshue, et al, "Hydrogenating Coal at 800 C," Bureau of Mines, U.S. Department of the Interior, Ind. Eng. Chem., 49, 2009, 1957.
9. R. W. Hiteshue, et al, "Hydrogenation of Coal to Gaseous Hydrocarbons," U.S. Department of the Interior, Bureau of Mines, Report of Investigations 6027, 1962.
10. M. J. Finn, G. Fynes, W. R. Ladner and J. O. H. Newman, "The Formation of BTX by the Hydropyrolysis of Coals," ACS Division of Fuel Chemistry Preprints, 24 (3), p 99-103, 1979.
11. J. R. Kershaw, G. Barrass and D. Gray, "The Effect of Catalyst Concentration, Temperature, and Residence Time on the Chemical Structure of Coal Hydropyrolysis of Oils," Coal Liquefaction Fundamentals, D.D. Whitehurst, Editor, ACS Symposium Series 139, ACS (1980).
12. P. C. Stangeby and P. L. Sears, "Rapid Pyrolysis and Hydropyrolysis of Canadian Coals," Final Report to the Energy Mines and Resources, Contract # OSU 76-00204, May 1978.

13. S. N. Basu and P. C. Strangeby, "A Study on the Rapid Devolatilization/Hydrogenation of Biomass Material, "ENFOR Report", March 1980.
14. K. M. Sprouse and J. K. Rosemary, "Coal Hydrogasification Process Development - Second Annual Technical Progress Report Government Fiscal Year 1980: Volume I: Peat Studies ET-3125-24, VOL II, UC-90, Rockwell International Energy Systems Group, Congo Park, California, October 20, 1980.
15. W. A. Fling, Jr., "Flash Hydropyrolysis of Western Kentucky No. 9 Bituminous Coal with Catalysts," DOE/ET/14943-T1 (NTIS 10/2/39), Cities Service Research and Development Company, Tulsa, Oklahoma, March 31, 1981.
16. M. Steinberg, P. T. Fallon and M. S. Sundaram, "Flash Pyrolysis of Coal with Reactive and Non-Reactive Gases, "DOE/CH/00016-1402 (NTIS-10/2/13), Brookhaven National Laboratory, Upton, N.Y., October 1, 1981 - September 30, 1982.
17. J. L. Beeson, D. A. Duncan and R. D. Oberle, "Flash Hydrogenation of Lignite and Bituminous Coal in An Entrained Flow Reactor," ACS Division of Fuel Chemistry Preprints, 24 (3), 72-81 (1979).
18. D. S. Scott and J. Piskorz, "Flash Pyrolysis of Biomass," Fuels from Biomass and Wastes, D. L. Klass and G. H. Emert, Editors, Proceedings: Chemical Congress of the North American Continent, 2nd, 1980, Held in Las Vegas, Nevada, Ann Arbor Science Publishers, 1981.
19. M. P. DuPlessis, "Coal Conversion Research". CIM Bulletin, February, 1981.
20. G. W. Taylor, "Liquid Fuels from Canadian Coals," CANMET Report 79-13, June 1979.
21. J. G. Speight, Upgrading Heavy Oils and Residua: The Nature of the Problem, "Catalysis on the Energy Scene", S. Kaliaguine and A. Mahay (Editors), Elsevier Science Publishers B.V., Amsterdam, 1984.
22. T. Aiba and H. Kaji, "Residue Thermal Cracking by the Eureka Process, "Chem. Eng. Prog., 77 (2), 37-44, 1981.
23. R. George, S. Ritchie, R. S. Roche and W. Steedman, "Pyrolytic Formation of n-Alkanes from Athabasca Asphaltenes", Chemistry and Industry, No. 1, 25-26, January 1979.
24. S. E. Moschopedis, S. Parkash and J. G. Speight, "Thermal Decomposition of Asphaltenes," Fuel, 57 (7), 431-434, 1978.

25. J. W. Bunger, D. E. Cogswell and A. G. Oblad, "Influence of Chemical Factors on Primary Processing of Utah Tar and Bibumen, American Chemical Society Division of Fuel Chemistry Preprints, 23 (4), 98-109, 1978.
26. K. Washimi, "Review of Studies on the Properties and Reaction Kinetics of Heavy Oil Thermal Cracking Residue," Future Heavy Crude Tar Sands, Int. Cont. 2nd., 1982, Edited by R. F. Meyer, J. C. Wynn and J. C. Olson, McGraw-Hill, N.Y., 1262-1267, 1984.
27. H. Honda, "Efficient Utilization of Petroleum Residue," J. Japan Petrol. Inst., 23 (1), 1-15, 1980.
28. V. Dang and M. Steinberg, "Coal Conversion in Flash Hydropyrolysis Reactors," BNL-26209 (NTIS 10/2/73), Process Science Division, Brookhaven National Laboratory, Upton, N.Y. May, 1979.
29. M. Sundaram, M. Steinberg and P. T. Fallon, "Flash Hydropyrolysis of Coal for Conversion to Liquid and Gaseous Fuels," DOE/METC/82-48 (NTIS 10/2/27), Process Sciences Division, Brookhaven National Laboratory, Upton, N.Y., May, 1982.
30. T. Suzuki et al., Ind. Eng. Chem. Process Des. Dev., 24, 149-154, 1982.
31. R. N. Pandey, "Development and Evaluation of Catalysts for Hydrogenation of Condensed Polynuclear Aromatic Compounds," Report to CANMET, File No. 15 SQ.23440-2-9185, 1985.
32. W. H. Calkins and R. J. Tyler, "Coal Flash Pyrolysis," Fuel, 63 (8), 1119-1124, 1984.
33. W. H. Calkins, E. Hagaman and H. Zeldes, "Coal Flash Pyrolysis," Fuel, 63 (8), 1113-1118, 1984.
34. D. E. Walsh and N. Chen, "Hydrogasification of Heavy Oils," Ind. Eng. Chem. Process. Des. Dev., 22 (3), 436-441, 1983.
35. M. A. Bergongnou et al., "Ultraflash Pyrolysis Process for Coal, Wood and Other Carbonaceous Materials," Coal: Phoenix of the 80's - Proceedings 64th CIC Coal Symposium, A.M. Al Taweel, Editor, Vol. 2, 523-529, 1981.
36. Z. J. Stoppel et al., "Structural Analysis of Tars from Fluidized Bed Pyrolysis of Coal. 1. Gas-Liquid Chromatography of Aliphatic and Aromatic Subfractions," Fuel, 61 (9), 817-823, 1982.

37. C. Y. Wen and S. tone, "Coal Conversion Reaction Engineering," in Chemical Reaction Engineering Reviews - Houston, D. Luss and V. W. Weekman, Jr., Editors, ACS Symposium Series No. 72, 56-109, ACS, 1978.
38. M. L. Selucky et al., "High Pressure Liquid Chromatography Fingerprinting of Petroleum and Petroleum Products," Fuel, 57 (10), 585-591, 1978.
39. J. L. Glajch, A. Lubkowitz and L. B. Rogers, "Pyrolysis Gas Chromatographic Applications to Coal Tar - and Petroleum Pitches," J. Chrom., 168 (35-364), 1979.
40. A. Matsunaga, "Separation of Aromatic and Polar Compounds in Fossil Fuel Liquids by Liquid Chromatography," Anal. Chem. 55, 1375-1379, 1983.
41. S. C. Ruckmick and R. J. Whitbise, "Liquid Chromatographic Systems for the Separation of Polycyclic Aromatic Hydrocarbons and Nitrogen Heterocycle Compounds Present in Coal Liquids," Journal of Chromatography, 321, 343-352, 1985.
42. C. Bollet et al., "Rapid Separation of Heavy Petroleum Products by High Performance Liquid Chromatography," Journal of Chromatography, 206, 289-300, 1981.
43. S. E. Moschopedis and R. W. Hawkins, "Fractionation of Oil Sands, Bitumen and Coal Derived Liquids," Inf. Ser. - Alberta Res. Council., 94, 17, 1981.
44. S. Asaoka, S. Nakata, Y. Shioto and C. Takeushi, ACS Div. Chem. Prepr., 26 (2), 412-430, 1981.
45. J. W. Bunger, D. E. Cogswell, R. E. Wood and A. G. Oblad, "Hydrolysis - Potential for Primary Upgrading of Tar Sand Bitumen," American Chemical Society Division of Fuel Chemistry Preprints, 25 (3), 369, 1981.
46. J. W. Bunger, D. E. Cogswell, R. E. Wood and A. G. Oblad, Oil Shale, Tar Sands, and Related Materials, H. C. Stauffer, Editor, Division of Fuel Chemistry Symposium, Second Chemical Congress, Las Vegas, Nevada, August 25-29, 1980, ACS Symposium Series 186, 1981.
47. J. W. Bunger, "Inhibition of Coke Formation in Hydropyrolysis of Residual Oils," American Chemical Society Division of Fuel Chemistry Preprints, 30 (3), 549-554, 1985.
48. A. E. George, B. B. Pruden and H. Sawatzky, "Effect of Hydrocracking Athabasca Bitumen on Sulphur-Type Distribution in the Naphtha Fraction," CANMET Report, 78-26, September 1978.

49. C. P. Khulbe et al., "Thermal Hydrocracking of Athabasca Bitumen: Effect of Recycle Gas Purity on Product Yields and Qualities," Proc.-Intersoc. Energy Convers. Eng. Conf., 13 (1), 342-349, 1978.
50. K. M. Jayakar et al., "Thermal Recovery of Oil from Tar Sands by An Energy-Efficient Process," Oil, Shale, Tar Sands, and Related Materials, H. C. Stauffer, Editor, ACS Symposium Series 163, 366-367, 1981.
51. M. Itoh, et al., "Catalytic Cracking of Heavy Oils in Combination with Pyrolysis for the Production of Light Oils," Ind. Eng. Chem. Process Des. Dev., 23 (3), 622-625, 1984.
52. R. George, S. Ritchie, R. S. Roche and W. Steedman, "A Pyrolysis Gas Chromatographic Analysis of Athabasca Bitumen," Ind. Eng. Chem. Prod. Res. Dev., 17 (4) 370-372, 1978.
53. W. Chen, et al., "Flash Hydrogenation of Coal," Fuel, 62 (1), 56-61, 1983.
54. A. J. Koplick et al., "Constitution of Tars from Flash Pyrolysis of Australian Coals," Fuel, 63 (11), 1570-1578, 1984.
55. S. W. Benson, "The Foundations of Chemical Kinetics", Chapter XIII 9, McGraw Hill Book Company, 1960.
55. J. Shabtai and R. Ramakrishnan, "Hydropyrolysis of Model Compounds", Adv. Chem., 183, 297-328, 1979.
57. R. George, S. Ritchie, et al., "Pyrolysis of Athabasca Tar Sands: Analysis of the Condensable Products from Asphaltene," Fuel, 58 (7), 523-530, 1979.
58. D. S. Ross and J. E. Blessing, "Possible Hydride Transfer in Coal Conversion Processes," Coal Liquefaction Fundamentals, D.D. Whitehurst, Editor, ACS Symposium Series 139, 301-313, 1980.
59. J. J. Ratto, et. al., "An Isotopic Study of the Role of a Donor Solvent in Coal Liquefaction," Coal Liquefaction Fundamentals, D. D. Whitehurst, Editor, ACS Symposium Series 139, 347-370, 1980.
60. D. C. Cronauer, et. al., "Isomerization and Adduction of Hydroaromatic Systems at Conditions of Coal Liquefaction," Coal Liquefaction Fundamentals, D. D. Whitehurst, Editor, ACS Symposium Series 139, 347-370, 1980.
61. J. M. L. Penninger and K. Versluis, "Thermal Cracking of Indan in Denterium at 8 MPa Pressure," Fuel, 61, (3), 283-290, 1982.

62. G. P. Curran, R. T. Struck and E. Gorin, Ind. & Eng. Chem. Proc. Des. & Dev., 6 (2), 166, 1967.
63. P. S. Virk, et. al., "Pericyclic Pathways in the Mechanism of Coal Liquefaction," Coal Liquefaction Fundamentals, D.D. Whitehurst, Editor, ACS Symposium Series 139, 329-345, 1980.
64. J. M. L. Penninger, H. W. Slotboom, H. W. Erdol and Kohle-Erdgas, Petrochemie Comb. with Brennstaff Chemie, 2b, 445, 1973.
65. G. E. Langlois and R. F. Sullivan, Adv. Chem. Ser., 97, 38, 1970.
66. S. A. Quader, Inst. Petrol., London, 59, 178, 1973.
67. R. P. Showronski and H. L. Recht, "Molten-Salt-Crystallized Hydrogenation of Phenanthrene," paper ORGN #170, 172nd ACS Natl. Mtg., San Francisco, Aug. 29 - Sept. 3, 1976.
68. M. V. C. Sekhar and M. Ternan, "Pyrolysis of Pitch Derived from Hydrocracked Athabasca Bitumen," Fuel, 58 (1-6; 92-98, 1979.
69. J. W. Bunger, et al., "Characteristics of Tar Sand Bitumen Asphaltenes and the Effect of Asphaltenes on Conversion of Bitumen by Hydropyrolysis," ACS Div. Petr. Chem. Prep., 24 (4), 1017-1027, 1979.
70. J. W. Bunger, "Reactions of Hydrogen During Hydropyrolysis Processing of Heavy Crudes," ACS Div. Petr. Chem. Prep., 30 (4), 658-663, 1985.
71. J. W. Bunger, "Inhibition of Coke Formation in Hydropyrolysis of Residual Oils," ACS Div. Petr. Chem. Prep., 30 (3), 549-554, 1985.
72. R. F. Probststein and R. E. Hicks, Synthetic Fuels, McGraw-Hill Book Company, 1982.
73. Discussion: "Upgrading of Petroleum Residues, Bitumen and Shale Oil, "Proceedings of the Eleventh World Petroleum Congress, Vol 4, 231-235, John Wiley and Sons Ltd. (1984)
74. R. A. Cardello, et al., "Catalytic Coal Gasification Development", Proceedings of the Eleventh World Petroleum Congress, Vol. 4, 265-273, John Wiley & Sons Ltd., 1984.
75. G. H. Dale, "Heavy Oil Cracking", Proceedings of the Eleventh World Petroleum Congress, Vo. 4, 83-94, John Wiley & Sons Ltd., 1984.

75. J. R. Murphy and E. L. Whittington, "Development of Reduced Crude Catalytic Cracking Technology, "Proceedings of the Eleventh World Petroleum Congress, Vol. 4, 15-24, John Wiley & Sons Ltd., 1984.
77. C. Takeuchi, Y. Fukui, Y. Shiroto and M. Nakamura, "Upgrading through Asphaltenic Bottom Conversion," Proceedings of the Eleventh World Petroleum Congress, Vol. 4, 187-197, John Wiley and Sons Ltd. (1984)
79. J. H. Shinn and T. Vermeulen, "High-yield Coal Conversion in a Zinc Chloride-Methanol Melt Under Moderate Conditions, Coal Liquefaction Fundamentals, D.D. Whitehurst, Editor, ACS Symposium Series 139, 226-242, 1980.
79. M. Morita, et al., "Kinetics of Direct Liquefaction of Coal in the Presence of Molybdenum-Iron Catalyst, Coal Liquefaction Fundamentals, D. D. Whitehurst, Editor, ACS Symposium Series 139, 213-226, 1980.
80. M. Nomura, et. al., "Hydrocracking of Athabasca asphaltene over $ZnCl_2$ - KCl - $NaCl$ melts with or without an additive of some transition metal chlorides," Fuel, 60 (8), 699-702, 1981.
31. C. P. Khulbe, B. B. Prudin and J. M. Denis, "Hydrocracking of Athabasca Bitumen: Effect of Coal-Base Catalyst on Pilot Plant Operation," CANMET (Canada Centre for Mineral and Energy Technology) Report No. 77-35, January 1977.
82. W. B. Russel and D. A. Seville, "Short Residence Time Hydrolysis of Coal, "DOE/ET.13153-T9 (NTIS-10/12/14), Department of Chemical Engineering, Princeton University, Princeton, NJ, October 1, 1979 - November 30, 1982.
83. D. G. Gavin, "Coal Hydrogenation Catalysis," Catalysis, Vol. 5, The Royal Society of Chemistry, Burlington House, London, 220-272, 1982.
84. T.S. Ma and Robert C. Rittner, "Modern Organic Elemental Analysis", Marcel Dekker, Inc., Chapter 6, p. 219, 1984.
85. American National Standard ANSI/ASTM D2887-73 (Reapproved 1978) pages 777-785.

IX APPENDICES

APPENDIX I

- o Literature Search and
Resources

Task 1: Literature Review

Introduction:

The primary objective of this literature search was to find literature and publications that pertained to the Flash Hydropyrolysis of Petroleum pitches that were published within the past ten years. Due to the lack of research done on this particular topic, related subjects were also pursued in the search. The systematic search included the Flash Hydropyrolysis of substances such as: coal, coal tar pitch, petroleum pitches, bitumen and heavy residuals. Other processes such as pyrolysis, cracking, hydrocracking and hydrogenation of the above were also included. Other subjects pursued in the search included pitch conversion, pitch utilization and simulated distillations. The library facilities at the University of Guelph, University of Waterloo, Ontario Research Foundation, Canada Institute for Scientific and Technical Information Centre, United States Department of Energy were used. The latter two contain the world's largest and comprehensive Energy Database (EDB) on fossil energy (coal, petroleum, natural gas, oil shale and tar sands) and alternative forms of energy sources. The database (EDB) covers energy related research in the basic sciences world wide including reports, journals, patents, translations, conference proceedings, and technical books.

Method of Search

There were four major sources of information for the library search. These sources were used in combination with indexes, which helped to find the locations of journals, conference proceedings and reports. The search method is described in the following:

1. Chemical Abstracts Search

Initially the Chemical Abstracts subject index was used. The following key headings were used: 1) Petroleum refining residues, 2) Pitch and 3) Coal. Pitch was further divided into two subheadings: (a) coal-tar pitch and (b) petroleum pitch. Under each of the headings and subheadings, key words were used to find appropriate references in the chemical abstracts. These are summarized in table 1, along with headings for simulated distillations. The collective subject index was used from the years 1976 to 1981, then, individual subject indices were used from 1982 to present. These indices included two volumes per year.

TABLE 1Chemical Abstract Search: Key Words

1. Petroleum Refining Residues

- o cracking
- o Hydrocracking
- o Thermal hydrocracking
- o Pyrolysis of
- o Hydropyrolysis of
- o pitch
- o upgrading of
- o conversion of
- o refining
- o flash hydropyrolysis of

2. Pitch

- (a) Petroleum Pitch
 - o flash hydropyrolysis
 - o hydropyrolysis
 - o pyrolysis
 - o cracking
 - o hydrocracking
 - o thermal hydrocracking
 - o upgrading
 - o conversion
 - o utilization
 - o gasification
- (b) Coal tar pitch
 - same key words as petroleum pitches

3. Coal

same as Petroleum Refining Residues

4. Distillation

- o simulated
- o pyrolysis
- o hydropyrolysis
- o gas chromatography

5. Gas Chromatography

simulated distillation

Once the appropriate references to the chemical abstracts were found in the indices, the abstracts were read and either recorded or eliminated depending on their relevance to the search. Relevant abstracts were recorded in the record book.

The abstracts referred to journals, conference proceeding, reports and patents. The location of the journals and proceedings, were found with the aid of two indices. One of which was useful in the translation of abbreviations into their full names, and the other gave the location of the journal or proceeding in Canadian libraries. The serials list on the microfiche gave the call numbers for any journal or proceeding located at the University of Guelph. A similar serials list did the same at the University of Waterloo. Journals or proceedings not available at Guelph or Waterloo were obtained through inter-library loan at the University of Guelph.

Proceedings and symposiums were often found as books in the regular stacks.

The majority of relevant reports and patents and other publications were obtained through inter-library services. Reports could be located by entering the title, author or corporate author of the report on the Geac computer at the University of Guelph.

2. Book Search

The subject mode of the Geac computer at the University of Guelph was used to locate any available books that pertained to pitches.

3. Computer Database Search

A computer search was done using the facilities at the University of Guelph to find all information within the past ten years that pertained to the following topics:

1. Flash hydropyrolysis of

- a) coal
- b) pitch
- c) bitumen
- d) heavy residuals

2. pitch conversion

3. pitch utilization

The following databases were used:

- | | |
|-------------|---------------------|
| o CAL | o ENERGYLINE |
| o SCISEARCH | o ENERGY NET |
| o NTIS | o COAL |
| o DOE | o ENGINEERING INDEX |

4. Specific Journal Search

Occasionally, a specific journal may contain a large portion of the information required. In the case of the pitch literature search, the journal, "Fuel," was very valuable. The key words used were similar to those used in the chemical index search. The fuel's cumulative index was used for the search.

APPENDIX II

- o Attempted Unsuccessful Method
of Analysis of Liquid Products

Attempted Unsuccessful Methods for Analysis of Liquid Products

Owing to a small quantities of liquid products, handling of micro-level products and analyses offered considerable difficulty. The attempted methods which led to the development of final method described in the text of this report, is presented here to reflect the nature of the problem and associated inaccuracies.

As discussed in section III under analyses of products the liquid products were trapped at -50°C in the coiled trap.

In preliminary runs the assembly shown in figure A.II.1 was used. This analytical system seemingly simple did not yield satisfactory results in routine analysis.

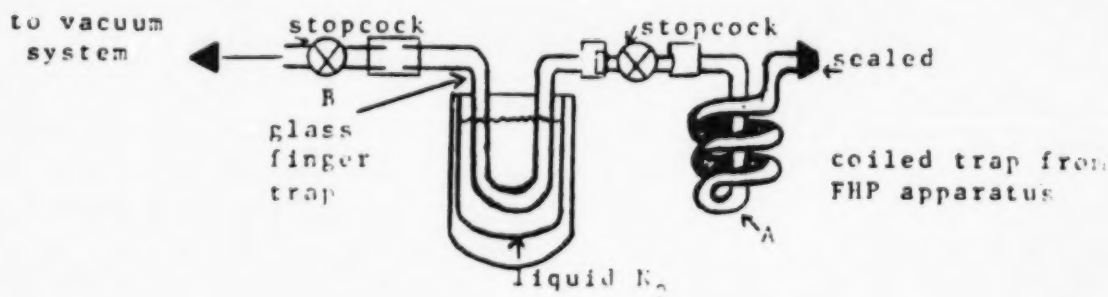


Figure A.II.1: The separation of low boiling liquid components from the coil trap.

In this method the coiled trap A (capturing total liquid products) was removed from the FHP apparatus and connected to glass finger trap B which in turn was connected to a vacuum system and cooled at liquid nitrogen. The connections were made from tygon tubings. The trap A was warmed to room temperature and the light products were vacuum distilled into the finger trap B. The contents of trap B were weighted to determine % light products. The contents of B are then extracted in known quantity of carbon disulfide solvent and injected into gas-chromatograph. The total weight of light products was calculated from the total area, by tacitly assuming FID response of average BTX to be same for various products.

The remaining heavy products of trap A was extraced with carbon disulfide, the solvent evaporated, contents weighed and the products subjected to elemental analysis. The two known amounts fractions was now combined for simulated distillation.

This analytical program seemingly simple was found tedious in practice.

* By raising the temperature of A, to a required degree, it is possible to transfer the entire product from A to trap B.

A summary of product separation scheme is given in figure A.II.2. A number of FHP runs were analyzed and results were found to be in random error greater $\pm 30\%$. For this reason this method of separation was discontinued and instead charcoal adsorption method was used for separation of light and high boiling components.

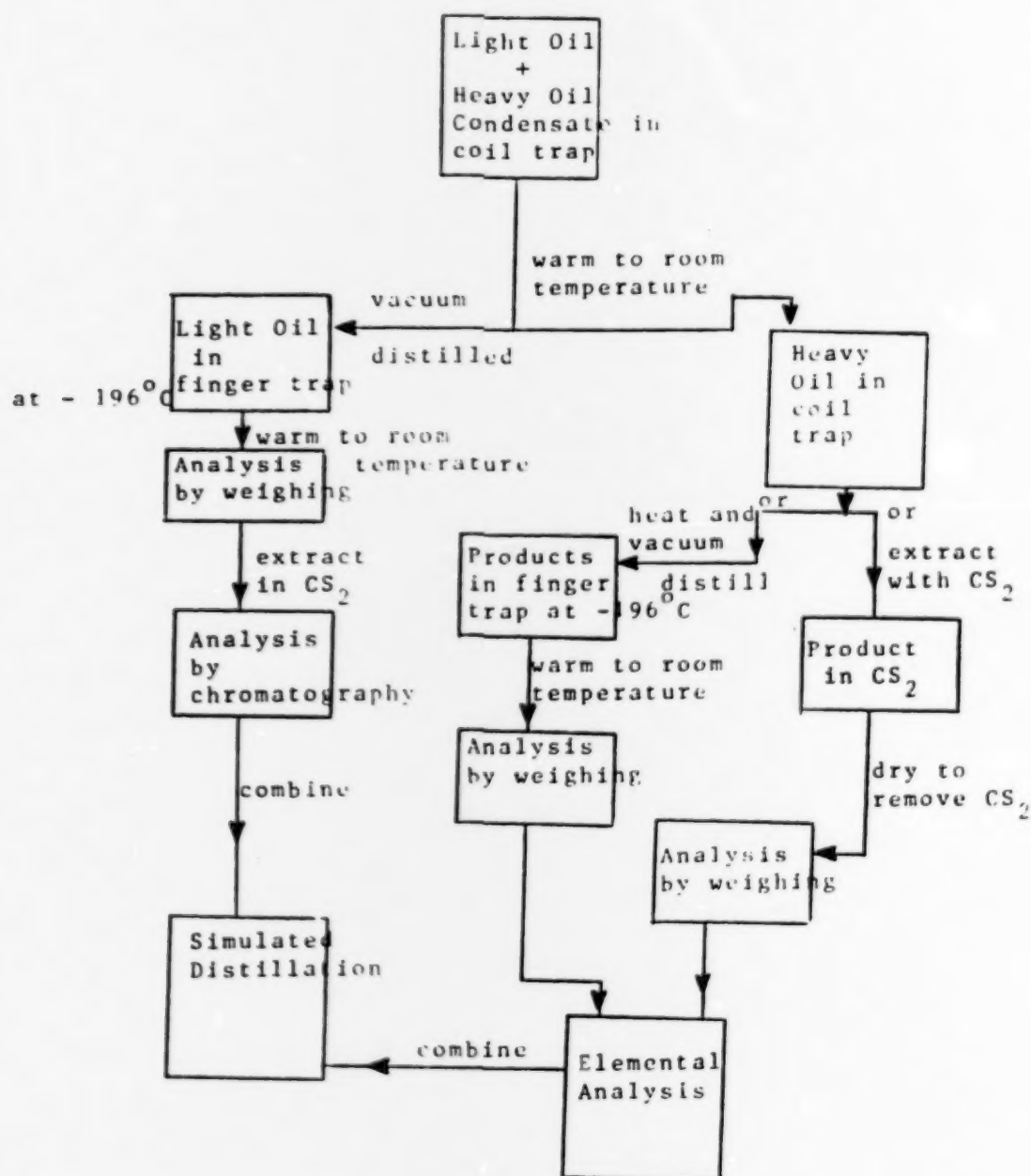


Figure A.II.2: A scheme of separation of light and heavy oil component of liquid products.